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**On the Viability of Nitronic Acids in the Decomposition of
Nitroaromatics: A Theoretical Study of Nitronic Acids**

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13. ABSTRACT (Maximum 200 words) The nitro <-> aci-nitro, keto <-> enol, and imine <-> enamine tautomeric processes in nitromethane, nitroacetaldehyde, and acetaldehyde were investigated at the G1 level of theory, in nitroacetaldehyde, 2-nitroacetaldehyde, and 3-nitropropene at MP4/6-31G*, in 2-nitroaniline, 2-nitrophenol, and 2-nitrotoluene at MP2/6-31G*, and in 2,6-dinitroaniline, 2,6-dinitrophenol, 2,6-dinitrotoluene, 2,4,6-trinitroaniline (picramide), 2,4,6-trinitrophenol (picric acid, PA), and 2,4,6-trinitrotoluene (TNT) at HF/6-31G*. These studies demonstrate that the ease of tautomerization is in the order PA (easiest), TNT then picramide, which parallels their sensitivity to impact. The nitronic acid tautomer of TNT is calculated at HF/6-31G* to lie 39 kcal/mol above TNT with a 65 kcal/mol barrier (with an extrapolated value of 48 kcal/mol under MP2), while the nitronic acid tautomer of picramide lies 48 kcal/mol above picramide beyond a 51 kcal/mol barrier. Cyclization and dehydration of the latter two nitronic acids should be overall exothermic processes.					
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PREFACE

This project was conducted under the direction of Dr. Koop Lammertsma in the Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294, under Contract F08635-90-K-0204 with Eglin Air Force Base, FL 32542-5910. Dr. Paul R. Bolduc managed the program for the Wright Laboratory / Armament Directorate. The program was conducted during the period from September 1, 1990 to January 31, 1993.

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LIST OF ABBREVIATIONS

Abbr.	Explanation
CAS	Complete Active Space
DSC	Differential Scanning Calorimetry
EPR	Electron Paramagnetic Resonance
G1	Gaussian 1
$H(r)$	total energy density
HF	Hartree-Fock
HLC	Higher Level Correlation
ICR	Ion Cyclotron Resonance
KDIE	Kinetic Deuterium Isotope Effect
MP#	Møller-Plesset at # order
MP(fc)	Møller-Plesset with frozen core
MP(full)	Møller-Plesset with all electrons
MRCI	Multi-Reference Configuration Interaction
PMP	Spin Projected MP
rms	Root Mean Square
QCI	Quadratic Configuration Interaction
QCISD(T)	Quadratic Configuration Interaction with Singles, Doubles, and partly Triples
TNT	2,4,6-Trinitrotoluene
ZPE	Zero Point Energy
$\rho(r)$	one-electron density distribution
$\nabla\rho(r)$	gradient vector field of ρ
$\nabla^2\rho(r)$	Laplacian of ρ
$\langle S^2,1 \rangle$	Expectation Value of the Spin Contamination

SECTION I

INTRODUCTION

The objective of this contract research was to provide more insight into the sensitivity of nitroaromatic compounds toward shock and impact by means of ab initio molecular orbital calculations on nitro and *aci*-nitro compounds. A specific task was to explore the relevance of *aci*-nitro derivatives in the decomposition pathway of nitroaromatics. The target systems selected by the Wright Laboratory / Armament Directorate of were trinitrotoluene (TNT), trinitrophenol (picric acid), and trinitroaniline (picramide) with the understanding that computational rigor might be limited for these large systems. The basis for the research was a tautomerism study on *o*-nitrophenol reported by Politzer and coworkers (Reference 1). Our approach to the relevance of nitro \rightleftharpoons *aci*-nitro tautomerism has been to delineate the computational aspect for this process "from the ground up." Therefore, we have studied the parent tautomeric processes (nitro \rightleftharpoons *aci*-nitro, imine \rightleftharpoons enamine, and keto \rightleftharpoons enol) in systems as simple as nitromethane, in composite nitroethylene systems, and in substituted nitroaromatics. This approach enabled us to set computational error bars for structural and energetic data and to make comparisons with experimental data. In addition to investigating the relevance of *aci*-nitro compounds, the primary focus, we have also touched upon their involvement in reaction pathways. Calculations have been conducted on a large number of systems that collectively lead to important observations. For clarity, we discuss in separate sections the parent tautomerisms, composite systems, and nitroaromatics. In this section we briefly describe relevant background data.

1 BACKGROUND

The question this project addresses is: why is picric acid more sensitive and picramide less sensitive than TNT, as measured by impact drop height, (i.e. 87 cm for picric acid, 177 cm for picramide, and 160 cm for TNT (Reference 2))? Thermochemical decompositions of TNT by isothermal differential scanning calorimetric (DSC) analyses gave primary kinetic deuterium isotope effects (KDIE) of 1.66 (245-269 °C) at induction and of 1.35 during the decay (References 3 and 4), which suggest that C—H bond rupture occurs in the rate-determining step. The induction activation energy for the decomposition of the liquid was estimated (from Arrhenius parameters) at 46.5 kcal/mol with a decay activation energy of 29 kcal/mol (Reference 4). C—NO₂ Bond fission is the preferred gas-phase decomposition process of mono- and dinitrotoluenes, using laser-powered homogeneous pyrolysis, with activation energies (from Arrhenius parameters) of ca. 70 kcal/mol (Reference 5). Incipient formation of anthranil occurs in the pyrolysis of *o*-nitrotoluene, using a single shock pulse tube (Reference 6); 2,4-dinitroanthranil is a known TNT decomposition product (Reference 7). Picosecond transient absorption studies of 2,4- and 2,6-dinitrotoluene solutions have suggested the formation of the *aci*-forms (Reference 8). Electron paramagnetic resonance (EPR) studies on the thermochemical decomposition of liquid TNT showed the formation of aryl benzyloxynitroxide radicals by intermolecular coupling (Reference 9). Using EPR, activation energies of 40.9 (30.2) kcal/mol for the induction (decay) were determined in the

thermochemical decomposition of TNT (Reference 10), which are similar to those determined by DSC.

Nitro \rightleftharpoons *aci*-nitro tautomerism was used by Politzer and coworkers (Reference 1) in a theoretical (HF/3-21G) study to interpret differences in sensitivities between hydroxy and amino substituted *o*-nitrobenzene. Cox and Hillier (Reference 11) reported on the *aci*-form of TNT at a rudimentary ab initio level (HF/STO-3G). Calculated geometries and energies of nitro compounds are, however, very sensitive to the theoretical levels employed. For example, Head-Gordon and Pople (Reference 12) calculated a 4.55 (7.2) kcal/mol NO₂-rotation barrier at MP2/6-311G** (HF) (Reference 13) for nitrobenzene while the experimental value is 2.9 kcal/mol; the HF-MP2/6-31G* geometry difference is small (Reference 14). This barrier amounts to 4.83 kcal/mol at QCISD(T)/6-311G** for nitroethylene at which level it is essentially the same as the experimental value of 5.05 kcal/mol; the HF-MP2/6-31G* geometry difference amounts to 5% (Reference 15). Bond dissociation energies are even more difficult to calculate. For example, the MRCI/6-31G**/CAS/6-31G* calculated CH₃-NO₂ \rightarrow CH₃-ONO rearrangement barrier is 10 kcal/mol too high (Reference 16). These examples illustrate the need for careful calibration of the theoretical methods.

2 COMPUTATIONAL METHODS

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 90/92 suite of programs (Reference 17). Structures were fully optimized within given symmetries with the split valence HF/3-21G basis, the heavy atom d-polarized HF/6-31G* basis (nitroaromatics) and MP2(full)/6-31G* (all other species), which includes the effects of all electron correlation using second-order Møller-Plesset perturbation theory. The identity of each structure was established at its highest level by determining the number of negative eigenvalues of the force constant matrix. These structures are also the basis for the frozen core MP4(fc) single point higher level calculations (for the smallest systems) that employ up to essentially a triply split basis set (6-311G) with d- and hydrogen p-polarization functions (**) and diffuse p- and s-functions (++); MP4(fc)/6-31G* was used for the nitroethylenes and MP2/6-31G* for the nitroaromatics. For the smallest species Gaussian 1 (G1) energies (equation 1) are reported except that 0.95 scaled MP2/6-31G* ZPEs are used.

$$G1 = MP4/6-311G^{**} + \Delta E(+) + \Delta E(2df) + \Delta E(QCI) + \Delta E(HCL) + \text{scaled ZPE} \quad [1]$$

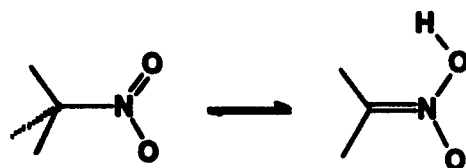
Bonding properties were investigated with Bader's topological one-electron density analysis (Reference 18) using optimized HF/6-31G* or MP2(full)/6-31G* wave functions. The one-electron density distributions $\rho(r)$ were analyzed with the aid of the gradient vector field $\nabla\rho(r)$ and the Laplacian $\nabla^2\rho(r)$, which also determines the regions in space wherein electronic charge is concentrated or depleted. Bond critical points have a minimum value in $\rho(r)$ along the maximum electron density path connecting two nuclei and are maxima in all other directions. The ellipticity ϵ at such a critical point describes the spatial symmetry of a bond, whereas the total energy density indicates a bond to be covalent ($H(r) < 0$) or ionic ($H(r) > 0$). The electron population of elements in structures (charges) were obtained by integration of the charge density within their respective basins as defined by the zero-flux surfaces.

SECTION II

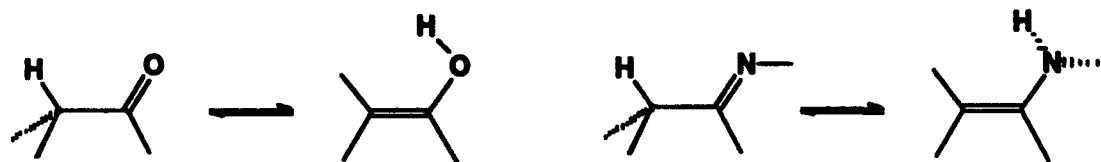
NITRO \rightleftharpoons *aci*-NITRO, KETO \rightleftharpoons ENOL, AND IMINE \rightleftharpoons ENAMINE TAUTOMERISM

1. INTRODUCTION

In order to establish the validity of *aci*-nitro compounds in the context of this research, it is of importance to determine at which levels of theory their structures and energies are calculated accurately. Nitronic acids are well known in organic chemistry, but a large energy difference of 21.8 kcal/mol for the nitromethane and *aci*-nitromethane tautomers was reported at MP2/6-31G* (Reference 19), which is for most organic systems a respectable level of theory. Similar observations are made for keto - enol tautomers, but here it has been shown that higher levels of theory reduce the energy difference between acetaldehyde and vinylalcohol from 16.4 kcal/mol at MP2/6-31G* to 10.4 kcal/mol at MP3/6-31++G** (Reference 20). We chose to use G1 theory to set a uniform standard and to determine the dependence of structures and energies on the levels of theory for the tautomerisms shown below.



nitro/*aci*-nitro



keto/enol

imine/enamine

2. NITRO \rightleftharpoons *aci*-NITRO TAUTOMERISM

We consider the nitromethane \rightleftharpoons *aci*-nitromethane tautomerism. Their structures and that of their common anion were optimized at all levels of theory of which the HF and MP2/6-31G* parameters are displayed in Figure 1. Total, relative, and ionization energies are listed in Tables 1-3, respectively. The properties of the bond critical points of some structures are provided. Atomic properties are shown in Figure 2.

a. Discussion

The MP2/6-31G* geometry of nitromethane is in good agreement with those obtained from microwave spectroscopy (assigned to 2, Reference 21) and single neutron diffraction data at 15 K (assigned to 1, Reference 22), but deviates slightly from a single crystal X-ray structure at 228 K (Reference 23), which is just below the melting point. These data do suggest that the N—O bond lengths calculated at MP2/6-31G* are ca. 0.015 Å too long. MP2 has a tendency to exaggerate the loss of charge density in the bonding region, and this effect is strongest for the NO bonds, i.e., the MP2-HF/6-31G* differences in bond lengths are $\Delta d_{\text{NO}} = 0.051$ Å. Similar observations are made for the harmonic frequencies, which underscores that the NO₂-group is the least well described at MP2/6-31G*. Electron density analysis of the bonds suggests that there is little if any hyperconjugation between the CH₃ and NO₂ groups, which is in line with the absence of a rotation barrier. From the G1 energies an atomization energy (ΣD_e) of -570.69 kcal/mol is calculated for nitromethane, which compares very well with -573.13 kcal/mol that is deduced from experimental heats of formation (Reference 24).

The *cis* and *trans* forms of *aci*-nitromethane differ in the orientation of the OH relative to the NO unit. The *trans* conformer has the higher dipole moment and is the transition structure for N—OH bond rotation (at MP2/6-31G*) with a barrier of 6.8 kcal/mol at G1. The MP2-HF geometrical differences are largely in the C=N and N—OH bonds. The electron density analysis shows *aci*-nitromethane to be strongly polarized with an essentially neutral nitrogen atom. The energy difference between this tautomer and nitromethane amounts to 14.1 kcal/mol at G1. This energy difference is significantly larger at lower levels of theory. For example, ΔE is 19.1 kcal/mol at MP4/6-311++G** + scaled ZPE, 22.9 kcal/mol at MP2/6-31G* (ZPE uncorrected), 20.3 kcal/mol at HF/6-31G*, and 0.3 kcal/mol at HF/3-21G.

Another measure for the accuracy of the calculations is the determination of proton affinities. The G1 calculated proton affinity of the nitromethide anion is 355.2 kcal/mol which compares very well with the experimentally determined ionization energy of 356.4 kcal/mol (gas phase, pulsed ICR, Reference 25) for nitromethane. The electron density analysis supports the contention that the strongly negatively charged oxygens are the most receptive toward protonation, which would render *aci*-nitromethane. The anion is a potential Y-aromatic system. However, the methylene group pyramidalizes (15.7°) using MP2/6-11+G* at which level the inversion barrier is a small 32 cal/mol.

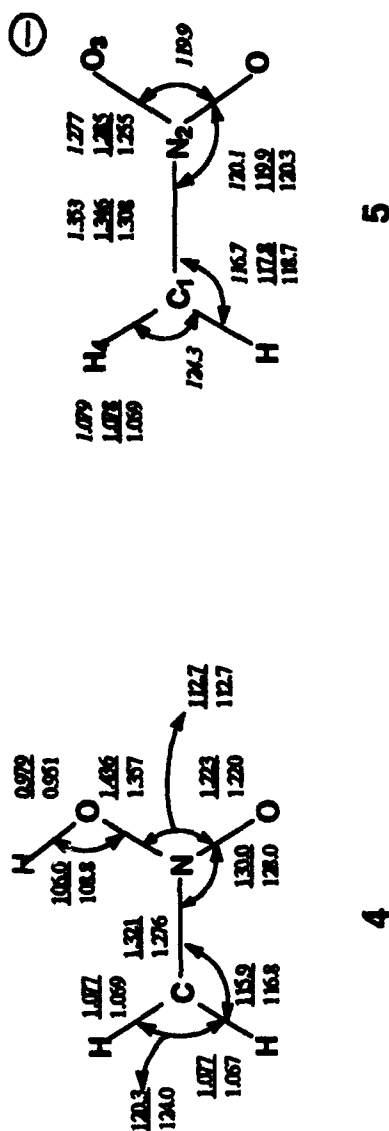
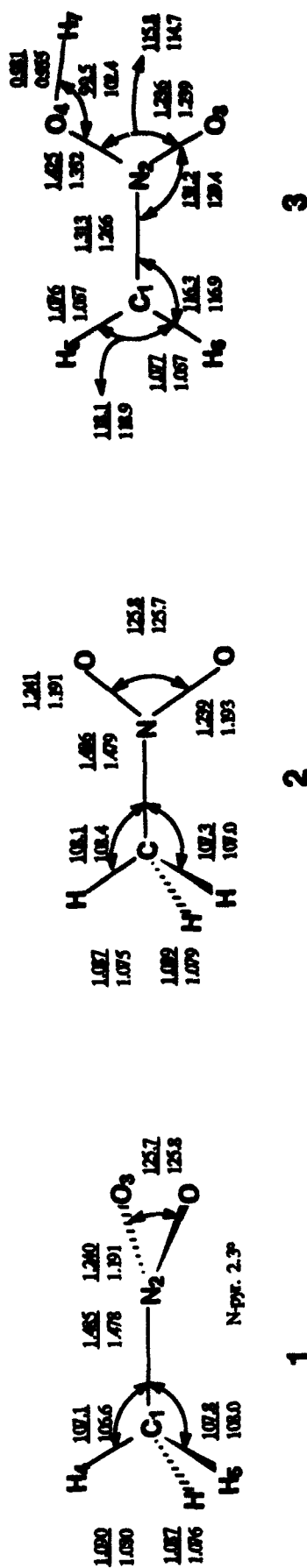


Figure 1. Optimized Nitromethane and *aci*-Nitromethane Tautomers and their Common Anion. The MP2/6-31G* Geometrical Parameters are underlined. The Lower Values are Those at HF/6-31G*. The Top Values in Italics are Those at MP2/6-311+G*.

TABLE 1. ABSOLUTE ENERGIES (in hartrees) OF NITROMETHANE, *act*-NITROMETHANE, AND THE NITROMETHIDE ANION.^a

Compound	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G**	MP4/6-311++G***	G1
1 C ₂	-242.25586 (0)	-243.66199 (0)	-244.34533 (0)	-244.37427	-244.52859	-244.67593
2 C ₂	-242.25585 (1)	-243.66198 (1)	-244.34531 (1)	-244.37425	-244.52855	-244.67603
3 C ₂	-242.25541 (0)	-243.62963 (0)	-244.30887 (0)	-244.33906	-244.49782	-244.65340
4 C ₂	-242.23161 (1)	-243.61350 (0)	-244.29632 (1)	-244.32636	-244.48722	-244.64260
5 C _{2v}	-241.66332 (0)	-243.05773 (0)	-243.73722 (0)	-243.76296	-243.93706	-244.10988

^a Number of imaginary frequencies is given in parentheses. ^b MP4(SDTQ) energies using MP2/6-31G* geometries.TABLE 2. RELATIVE ENERGIES (in kcal/mol) FOR NITROMETHANE, *act*-NITROMETHANE, AND THE NITROMETHIDE ANION.

Compound	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	MP4/ 6-31G*	MP4/ 6-311++G**	MP4/ (+ ZPE)	G1
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.01	0.01	0.01	0.01	0.03	-0.02	-0.06
3	0.27	20.31	22.88	22.09	19.30	19.09	14.14
4	15.21	30.43	30.76	30.05	25.95	25.34	20.91

TABLE 3. IONIZATION ENERGIES (in kcal/mol) FOR NITROMETHANE AND *act*-NITROMETHANE.

Reaction	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	MP4/ 6-31G*	MP4/ 6-311++G**	MP4/ (+ ZPE)	G1	Expt.
1→5	371.8	379.2	381.6	383.6	371.2	362.7	355.2	356.4
3→5	371.6	388.9	358.7	361.5	351.9	343.7	341.1	—

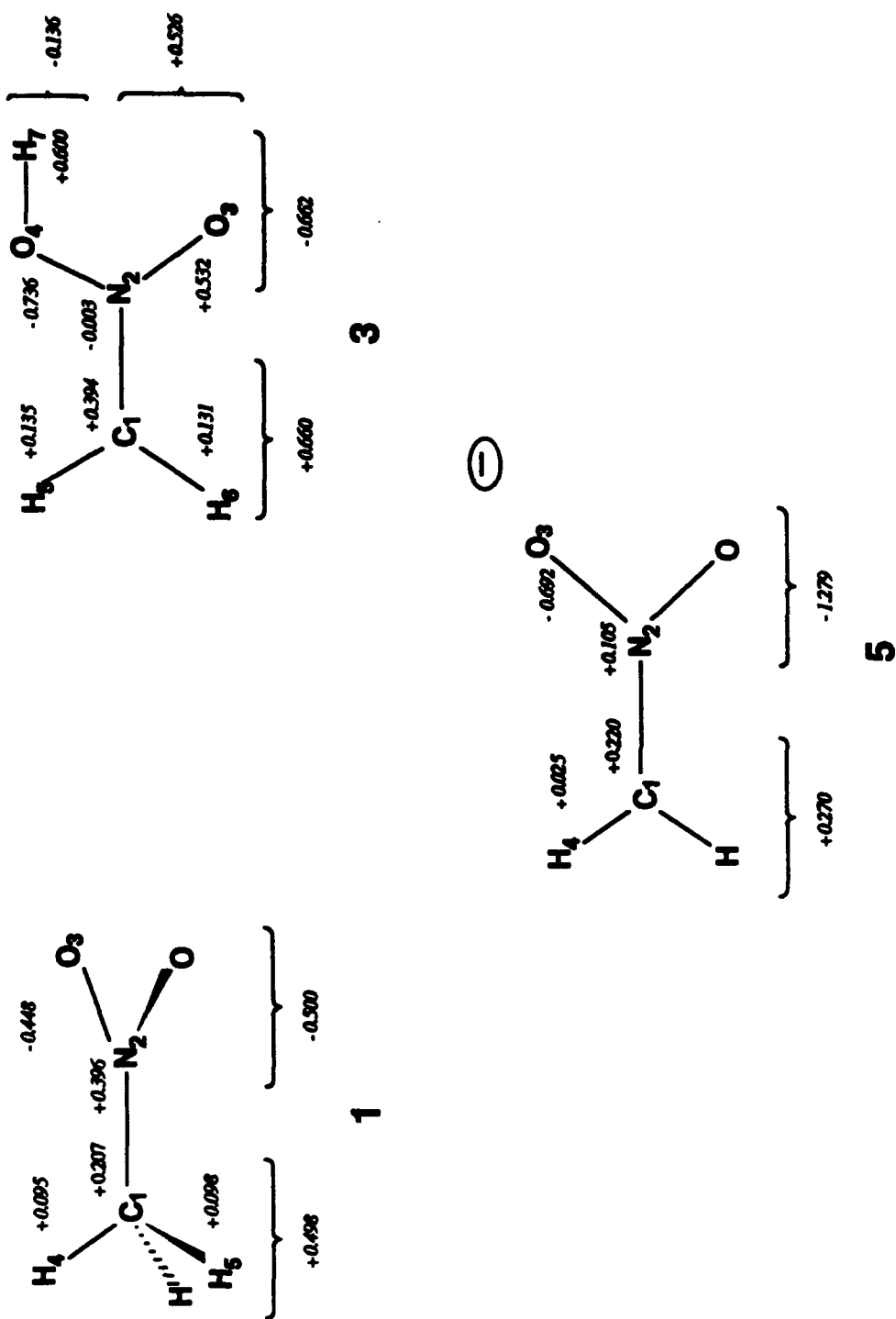


Figure 2. Atomic and Group Charges for the Nitromethane and *aci*-Nitromethane Tautomers and their Common Anion.

3. KETO \rightleftharpoons ENOL AND IMINE \rightleftharpoons ENAMINE TAUTOMERISM

The parent acetaldehyde \rightleftharpoons vinyl alcohol and acetaldimine \rightleftharpoons vinyl amine tautomerisms are considered. Their structures and those of their conformers and anions were optimized at all levels of theory of which the HF and MP2/6-31G* parameters are displayed in Figure 3. Total, relative, and ionization energies are listed in Tables 4-6, respectively. Atomic properties are shown in Figure 4. Harmonic frequencies are listed in Table 7.

a. Discussion

The MP2/6-31G* structures compare well with those available experimentally. This is the case for acetaldehyde (Reference 26), vinyl alcohol (microwave spectrum, Reference 27), acetaldimine (microwave spectrum (Reference 28) and gas phase (Reference 29) and matrix IR spectra (Reference 30)) and vinyl amine (microwave spectrum, Reference 31). The HF-MP2/6-31G* difference in geometrical parameters is largest for C—O, C=O, C—N, C=N, and C=C bonds. The rms differences between experimental and 0.95 scaled MP2/6-31G* harmonic frequencies are 28 cm⁻¹ for acetaldehyde (Reference 32), 27 cm⁻¹ for vinyl alcohol (Reference 33), 30 cm⁻¹ for acetaldimine (Reference 29), 52 cm⁻¹ for vinyl amine (Reference 34), which may suggest that acetaldimine and vinyl amine are the least well described experimentally.

Vinyl alcohol has two conformers of which the *syn* form is 0.9 kcal/mol (G1) more stable than the *anti* conformer. In contrast, *anti*-acetaldimine is 0.9 kcal/mol more stable than the *syn* form (MP4/6-311++G**), which agrees with the experimental value of ca. 2 kcal/mol (Reference 35), and corrects earlier theoretical data (Reference 36). Vinyl amine is calculated to be non-planar with an N-inversion barrier of 1.4 kcal/mol (MP4/6-311++G**), which agrees well with the best experimental estimates of 1.1 kcal/mol (Reference 37). The anion of acetaldimine prefers the *syn* conformation over the *trans* form by 0.8 kcal/mol (G1).

The G1 energy difference between the acetaldehyde and vinyl alcohol tautomers is 10.9 kcal/mol, which compares well with the estimated gas phase value of 9.9 kcal/mol. A much smaller energy difference of 3.8 kcal/mol (G1) is calculated for the acetaldimine and vinyl amine tautomers, for which no experimental value is available.

The theoretically estimated atomization energy of - 641.4 kcal/mol (G1) for acetaldehyde is in good agreement with the experimental value of - 642.5 kcal/mol (Reference 38). The G1 theoretical estimate for the atomization energy of acetaldimine is - 694.3 kcal/mol, which differs significantly from the experimental value of - 708.7 kcal/mol. The theoretical estimate for the ionization of acetaldehyde is 365.0 kcal/mol, which is in good agreement with the gas phase value of 366.4 \pm 3 kcal/mol (Reference 39). Likewise, the calculated ionization energy of 354.1 kcal/mol for *syn*-vinyl alcohol compares well with the experimental value of 356.6 kcal/mol. The G1 estimated ionization energies are 377.3 kcal/mol for *anti*-acetaldimine and 373.5 kcal/mol for vinyl amine, but no experimental data are available. For comparison, the gas phase ionization energy of propene is 390 \pm 3 kcal/mol.

Possible internal Coulombic (- + -) stabilization of the acetaldehyde and acetaldimine anions was evaluated by means of MP2/6-31G* atomic charges which are displayed in Figure 4. The negative charge is similarly distributed over the CH₂ and CHNH or CHO groups. The

accumulation of charge for the CH_2 group, as based on the same group in vinyl alcohol/amine, is comparable to the accumulation of charge in the CHNH/CHO group, as based on the same group in acetaldehyde/acetaldimine. From this, the similar heavy atom polarization in the neutrals and anions, and the fact that nearly the full unit of negative charge can be accounted for in the hydrogens, it seems that the anions do not experience a strong charge (- +) effect (Reference 20 and 40). The calculations are more suggestive of extended conjugation.

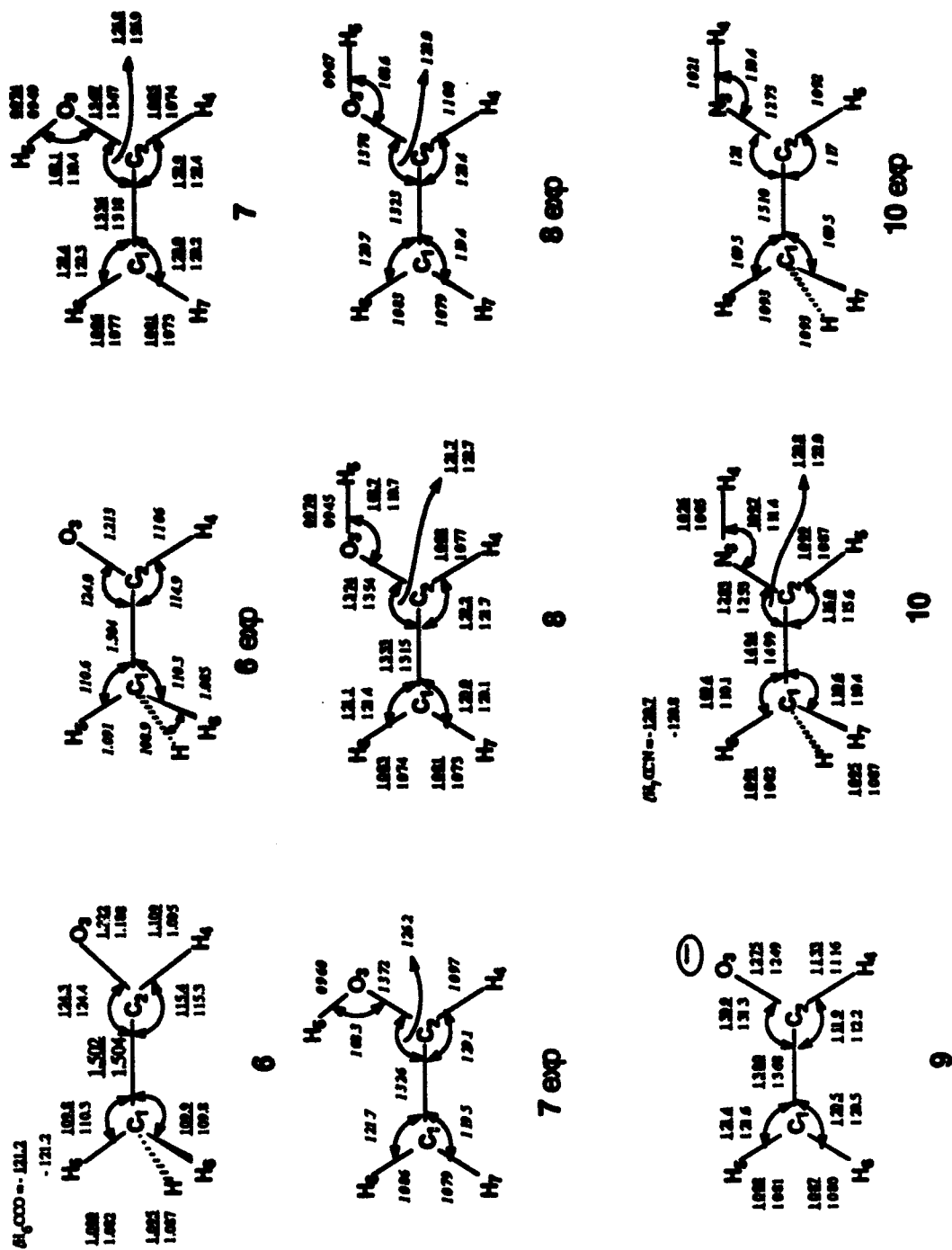


Figure 3. Optimized Acetaldehyde/Vinyl Alcohol and Acetaldehyde/Vinyl Anion Tautomers and their Anions. The MP2/6-31G* Geometrical Parameters are Underlined. The Lower Values are Those at HF/6-31G*. Experimental Values are Given in Italics in Separate Structures.

TABLE 4. ABSOLUTE ENERGIES (in - hartrees) OF THE KETO/ENOL AND IMINE/ENAMINE TAUTOMERS AND THEIR ANIONS.^a

Compound	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G**	MP4/6-311++G**	G1 ^b
6 C _s	152.05525 (0)	152.91597 (0)	153.35897 (0)	153.38701	153.49507	153.48768
7 C _s	152.04177 (0)	152.88889 (0)	153.33216 (0)	153.35960	153.47428	153.55607
8 C _s	152.03690 (0)	152.88539 (0)	153.32840 (0)	153.35600	153.47198	153.55467
9 C _s	151.42195 (0)	152.28393 (0)	152.73454 (0)	152.75952	152.89241	152.99181
10 C _s	132.32300 (0)	133.07384 (0)	133.50376 (0)	133.53656	133.63670	133.69345
11 C _s	132.32262 (0)	133.07280 (0)	133.50272 (0)	133.53579	133.63535	
12 C ₁		133.06196 (0)	133.49128 (0)	133.52299	133.62809	133.68737
13 C _s	132.32644 (0)	133.05920 (1)	133.48820 (1)	133.51917	133.62453	
14 C _s	131.66751 (0)	132.42189 (0)	132.85910 (0)	132.88859	133.01525	133.09346
15 C _s	131.65876 (0)	132.41544 (0)	132.85267 (0)	132.88213	133.01191	133.09214

^a Values in parentheses are the number of imaginary frequencies. ^b MP2/6-31G* geometries.

TABLE 5. RELATIVE ENERGIES (in kcal/mol) OF THE KETOENOL AND IMINE/ENAMINE TAUTOMERS AND THEIR ANIONS.

Compd	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	MP4/6-311++G** + ZPE corr.	C1
Acetaldehyde/Vinyl alcohol						
6	0.00	0.00	0.00	0.00	0.00	0.00
7	8.46	16.99	16.82	17.20	13.29	10.90
8	11.51	19.20	19.18	19.46	14.39	11.78
Acetaldimine/Vinyl amine						
10	2.16	0.00	0.00	0.00	0.00	0.00
11	2.39	0.65	0.66	0.46	0.48	—
12	—	7.46	7.83	8.52	5.40	3.82
13	0.00	9.18	9.76	10.91	7.64	—

TABLE 6. IONIZATION ENERGIES (in kcal/mol) OF THE KETOENOL AND IMINE/ENAMINE TAUTOMERS.

Compd	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	MP4/6-311++G**	MP4/6-311++G** + ZPE corr.	G1
Acetaldehyde/Vinyl alcohol							
6 → 9	397.40	396.61	391.84	393.76	378.18	369.66	364.98
7 → 9	388.94	379.62	375.01	376.56	365.13	356.61	354.08
Acetaldimine/Vinyl amine							
10 → 14	411.33	409.10	404.53	406.61	389.97	380.68	376.50
10 → 15	416.82	413.15	408.56	410.66	392.06	382.49	377.33
12 → 14	413.49 ^a	401.65	396.70	398.09	384.56	375.20	372.68
12 → 15	418.98 ^b	405.70	400.73	402.15	386.66	377.02	373.51

^a Represents 13 → 14. ^b Represents 13 → 15.

TABLE 7. CALCULATED MP2/6-31G* AND EXPERIMENTAL FREQUENCIES (in cm⁻¹) FOR THE KETO/ENOL AND IMINE/ENAMINE TAUTOMERS.^a

Acetaldehyde 6			syn-Vinyl alcohol 7			anti-Acetalimine 10			Vinyl amine 12		
calcd	description ^c	exptl ^e	calcd	description ^d	exptl ^e	calcd	description ^f	exptl ^f	calcd	description ^g	exptl ^g
3073	CH ₃ str a' 6	3014	3556	OH str a' 34	3580 ^b	3292	NH str a' 2		3496	NH ₂ str 10	
3026	CH ₃ str a" 6	2964	3168	CH ₃ str a' 7	3130	3066	CH ₃ str a' 7	2988	3389	NH ₂ str 9	
2950	CH ₃ str a' 6	2923	3110	CH str a' 7	3096	3023	CH ₃ str a" 12		3161	CH ₃ str 10	
2840	CH str a' 121		3067	CH ₃ str a' 5		2951	CH str a' 54	2916	3073	CH str 7	
1712	CO str a' 98	1746	1655	CC str a' 126	1649 ^d	2937	CH ₃ str a' 54	2886	3062	CH ₃ str 10	2982 ^e
1459	CH ₃ def a" 11	1436	1419	CH ₃ scl a' 17	1421 ⁱ	1644	CN str a' 9	1651	1673	CC str 100	1670 ^e
1451	CH ₃ def a' 18	1430	1322	CH rock a' 1	1310	1465	CH ₃ def a" 9		1619	NH ₂ scl 29	1625 ^e
1395	CH bend a'13	1395	1291	CH* bend a' 6	1282	1462	CH ₃ def a' 100	1454	1422	CH ₃ scl 2	1454
1368	CH ₃ def a' 18	1353	1089	COH bend a' 188	1111 ^h	1402	CH ₃ def a' 17		1303	CH bend 7	
1112	CH ₃ rock a" 1	1107	955	CH wag a" 36	973 ⁱ	1369	CH* bend a' 14	1359	1261	CCN scl 26	1254 ^e
1110	CC str a' 22	1114	932	CH ₃ rock a' 9	952	1246	CNH bend a' 37	1250	1052	NH ₂ rock 9	1080 ^e
880	CCO str a' 6	877	765	CH ₃ wag a" 64	819	1090	CN tor a" 4	1102	964	CH wag 27	1043 ^e
760	CH ₃ twist a" 1	764	687	CH ₃ twist a" 1	711 ^m	1058	CH ₃ rock a" 17		934	CH ₃ rock 2	
490	CCO bend a' 13	506	471	CCO bend a' 14	516	1039	CH ₃ rock a' 27	1040	762	CH ₃ wag 63	809 ^e
144	CC tor a" 1	143	448	CO tor a" 132	475	915	CC str a' 6		740	NH ₂ wag 189	650 ^e
						665	CH* OP a" 61	654	626	CC tor 161	575 ^e
						473	CCN bend a' 18		449	CCN bend 4	
						179	CC tor a" 1		332	CN tor 57	

^a The calculated frequencies are uniformly scaled by a 0.95 factor. ^b The main characteristics of the normal modes are given. For more detailed descriptions see the listed references ^c Reference 22. ^d Reference 33. ^e Reference 29. ^f Reference 34. ^g Observed 3576 and 3584. ^h Additional freq. at 1608. ⁱ Additional freq. at 1404. ^j Observed 1109 and 1112. ^k Observed 970 and 975. ^l Observed 708 and 713. ^m Observed 2976 and 2987. ⁿ Observed 1668 and 1672. ^o Uncertain assignment. ^p Observed 1248 and 1260. ^q Observed 1078 and 1084. ^r Observed 1039 and 1046. ^s Observed 805 and 812. ^t Observed 616 and 684. ^u Observed 569 and 580.

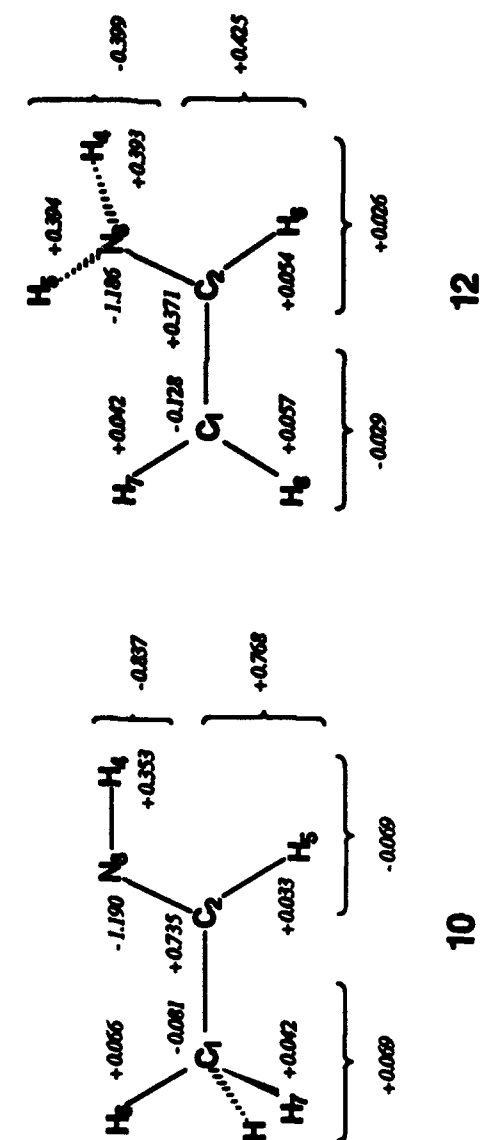
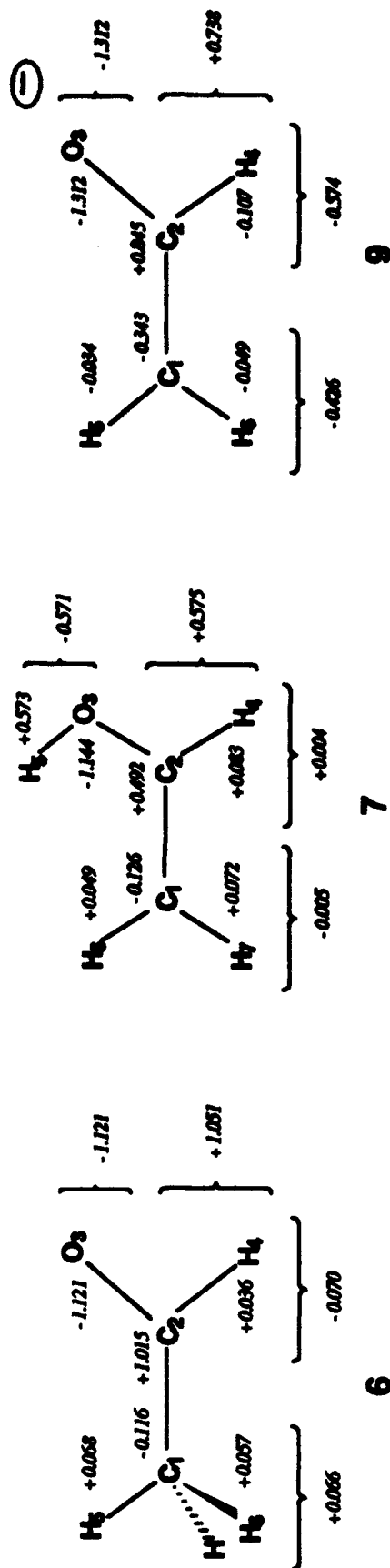


Figure 4. Atomic and Group Charges for Keto/Enol and Imine/Enamine Tautomers and their Anions.

SECTION III

TAUTOMERISM IN SUBSTITUTED NITROETHYLENES

1. INTRODUCTION

We consider the *cis* isomers of 2-nitrovinyl alcohol, 2-nitrovinyl amine and 1-nitropropene and their tautomers. Two sets of tautomers are possible for each. Important for this research are the nitro \rightleftharpoons *aci*-nitro tautomers where the hydrogen is transferred from the OH, NH₂, and CH₃ substituents. These represent symmetry allowed [1,5]-H shifts and are examples of conjugate tautomerism. The other tautomeric processes display [1,3]-H transfers (as in Section II), and these are better conducted in an acid/base exchange environment.

The structures of all tautomers were optimized at all levels of theory of which the HF and MP2/6-31G* parameters are shown in Figure 5 to display the effects of basis sets and electron correlation. The MP2/6-31G* structures for the tautomeric pairs and their transition structures are shown in Figures 6-8. Total and relative energies are listed in Tables 8 and 9, respectively, and visualized in Figure 9. A comparison of MP4/6-31G* energies between the conjugated tautomers and their parents is given in Figure 10. Atomic properties are shown in Figures 11 and 12, which display bond critical point data and total electron densities, respectively.

2. DISCUSSION

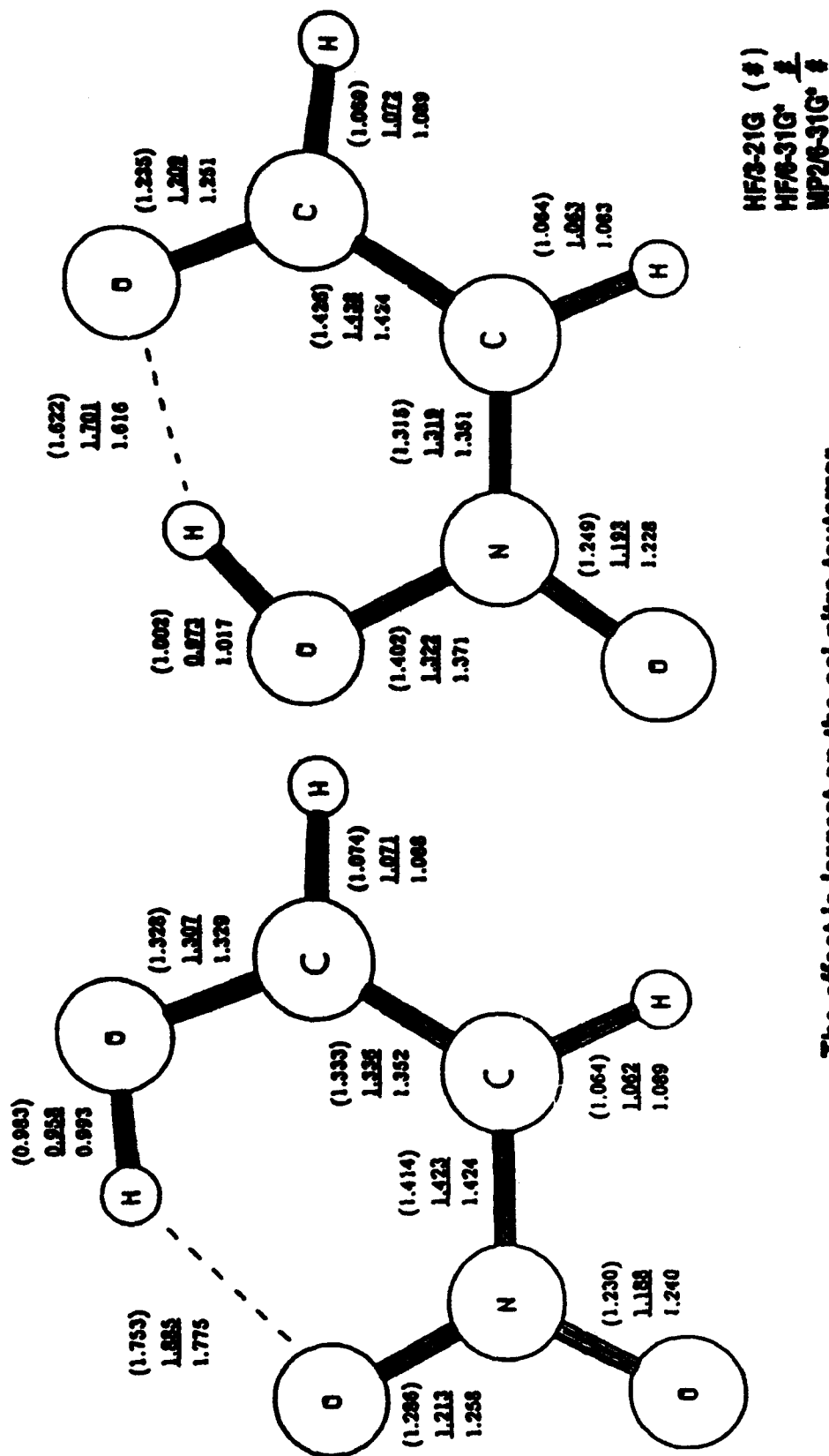
The structural parameters highlight significant differences between HF/3-21G and HF/6-31G structures, underscore the importance of the effects of electron correlation in the geometry optimizations, and compare well with the limited literature data (Reference 41).

The *cis* OH and NH₂ substituted nitroethylenes are well set up for tautomerism. In fact, the separation between the OH hydrogen and the neighboring NO₂ oxygen in 16 is only 1.775 Å, and that between one of the NH₂ hydrogens and the NO₂ oxygen in 21 is 1.992 Å. Both the (O)NO...HO (Figure 12) and (O)NO...HNH interactions represent hydrogen bonding as confirmed by the Bader electron density analysis which identifies their bond critical points (Figure 11). This is also the case for their nitronic acids which have very short hydrogen bonds of 1.616 Å for (O)NOH...O and 1.606 Å for (O)NOH...NH. 1-Nitropropene has a bisected conformation of the methyl group (Figure 8). The eclipsed form 26a represents the transition for CH₃-rotation (except at 3-21G), the barrier of which amounts 0.6 kcal/mol (MP4/6-31G*), and consequently the two (O)NO...H₂CH distances are longer. Its nitronic acid tautomer 27 has a conformation in which the *aci*-nitro hydrogen is anti to the methylene group and thereby contrasts the keto (17) and imine (22) analogues, which have corresponding *syn* conformations for their *aci*-nitro hydrogens. From a comparison of C=C bond lengths with those of ethylene (1.335 Å) and nitroethylene (1.329 Å), it appears that the nitro group strengthens the olefinic bond whereas it is weakened by the additional substituents OH, NH₂, and to a smaller degree CH₃. This effect may reflect extended conjugation.

The energy difference between the 2-nitrovinyl alcohol and *aci*-nitroacetaldehyde tautomers is only 4.8 kcal/mol with a small barrier of 5.8 kcal/mol for the forward reaction. A significantly larger energy difference of 14.5 kcal/mol is calculated for the 2-nitrovinyl amine and *aci*-nitroacetaldimine tautomers, of which the latter has a kinetic stability of only 2.2 kcal/mol at MP4/6-31G* but none when zero-point energy corrections are included. 1-Nitropropylene is 18.7 kcal/mol more stable than its nitronic acid and would minimally require a large 42.4 kcal/mol for such a rearrangement to occur. Figure 9 illustrates not only the large differences between these isoelectronic systems but also lists the significant dependency of energy differences on the theoretical levels employed. The tendency for tautomerism appears to decrease both kinetically and thermodynamically on introducing the substituents in the order OH, NH₂, and CH₃. It is recognized that the MP4/6-31G* level of theory is not adequate for a final evaluation of the potential energy surface (see Section II) and hence these energy differences are likely to reduce at more sophisticated levels.

Competing tautomers are those resulting from formal [1,3]-H shifts and these are 2-nitroacetaldehyde, 2-nitroacetaldimine, and 3-nitropropene. Their MP4/6-31G* (+ ZPE) energy differences with the nitroethylene tautomers are - 3.6, +2.4, and +1.1 kcal/mol respectively. This means that in these systems the keto \rightleftharpoons enol energy differences amounts to only 4.0 kcal/mol, whereas it is 17.2 kcal/mol for acetaldehyde \rightleftharpoons vinyl alcohol at the same level of theory. Considering that this latter value reduces to 10.9 kcal/mol at G1, and applying this 'correction' also to the conjugated analogue leads to the likely conclusion that 2-nitrovinyl alcohol is the global minimum. The same argument applies to the other compounds and these are summarized in Figure 10.

The Effects of Electron Correlation on Geometries



The effect is largest on the aci-nitro tautomer

Figure 5. Structures of the Tautomers of Nitrovinyl Alcohol.

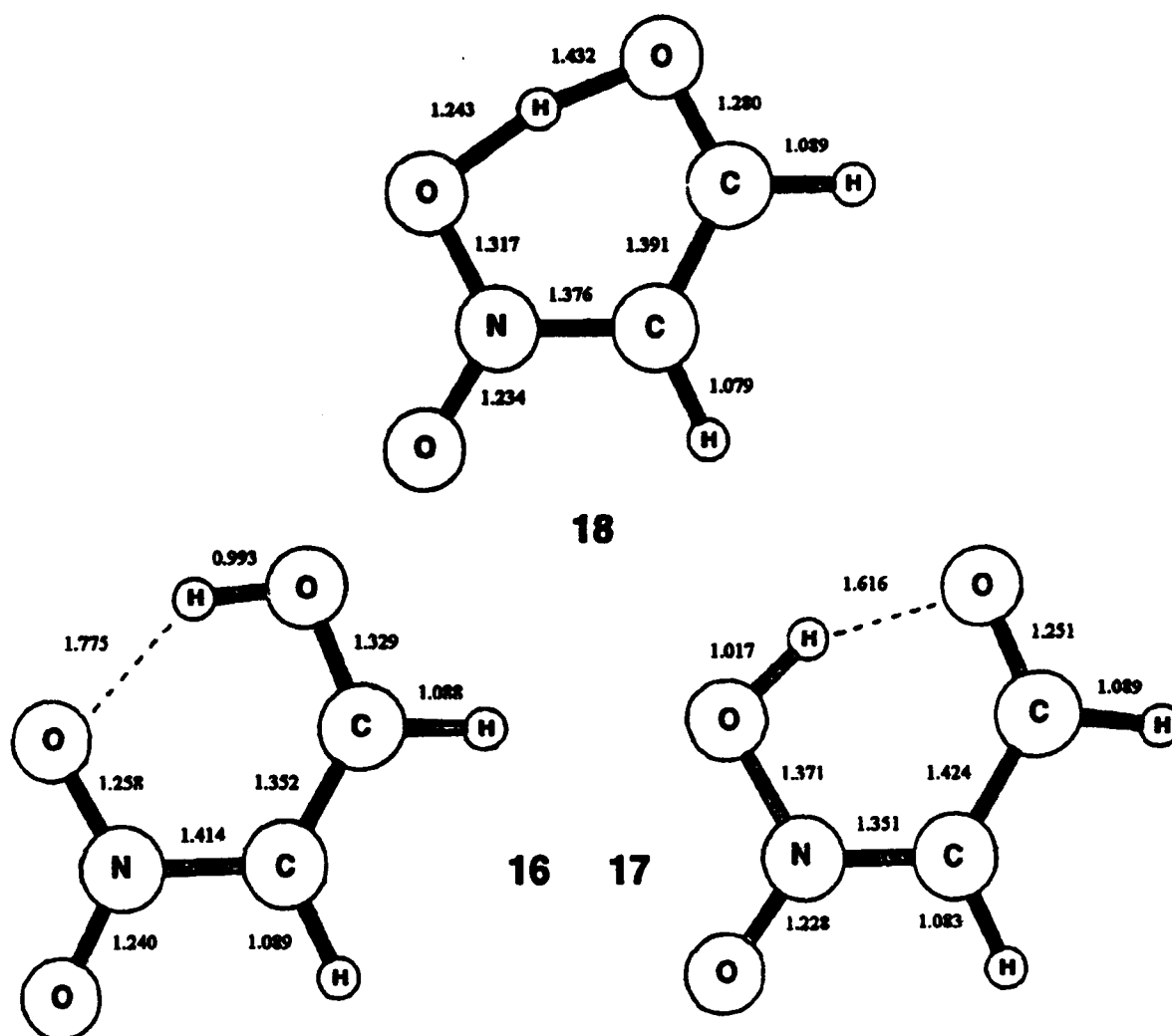


Figure 6. MP2/6-31G* Structures of the cis Tautomers of 2-Nitrovinyl Alcohol and their Transition Structures.

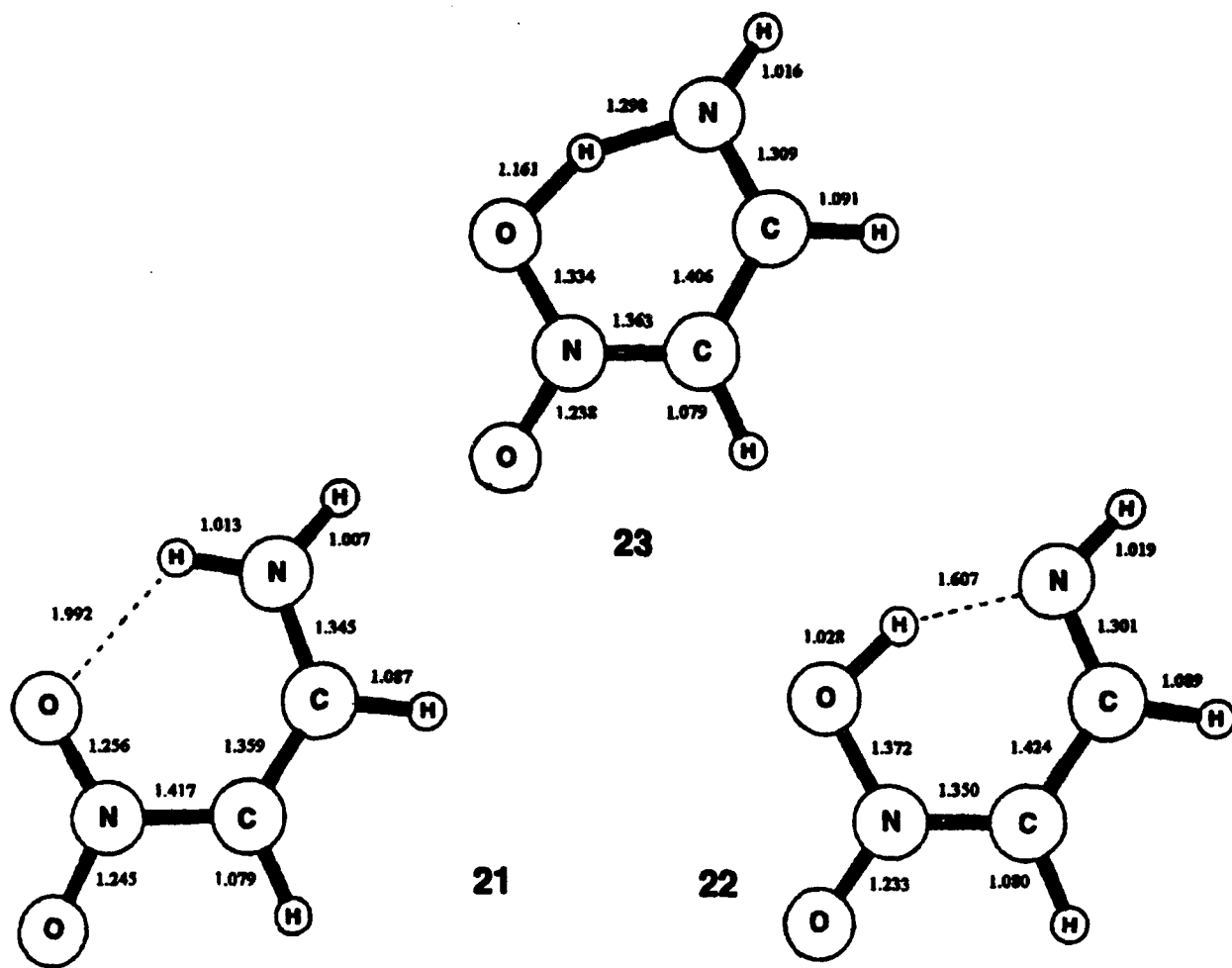


Figure 7. MP2/6-31G* Structures of the cis Tautomers of 2-Nitrovinyl Amine and their Transition Structures.

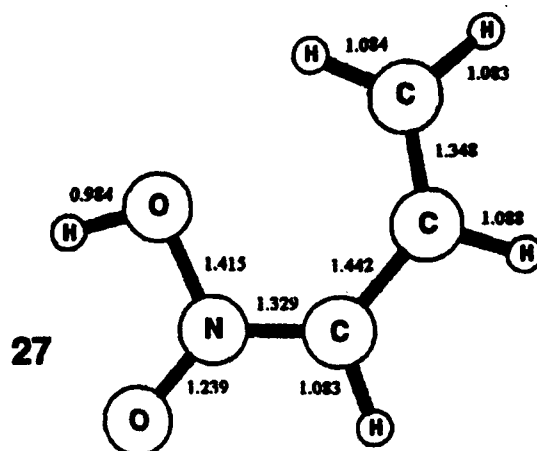
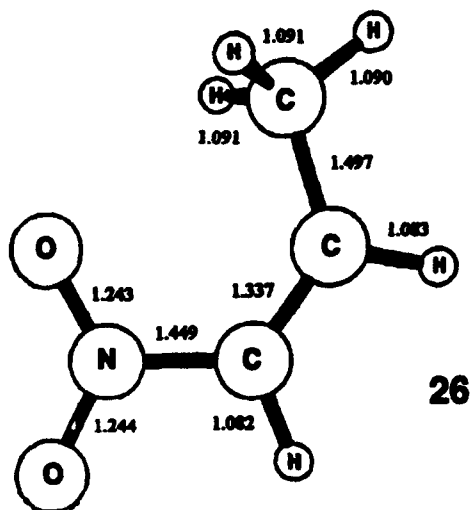
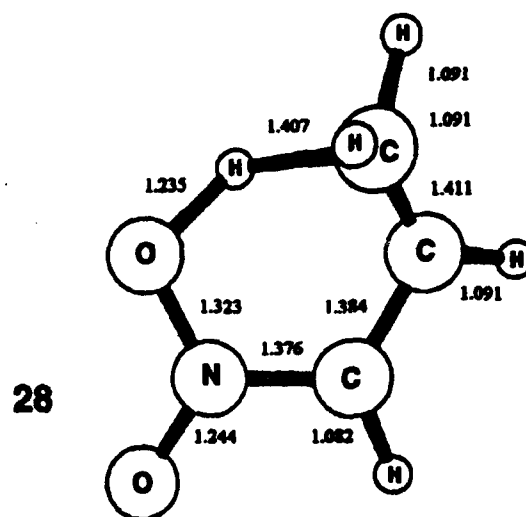
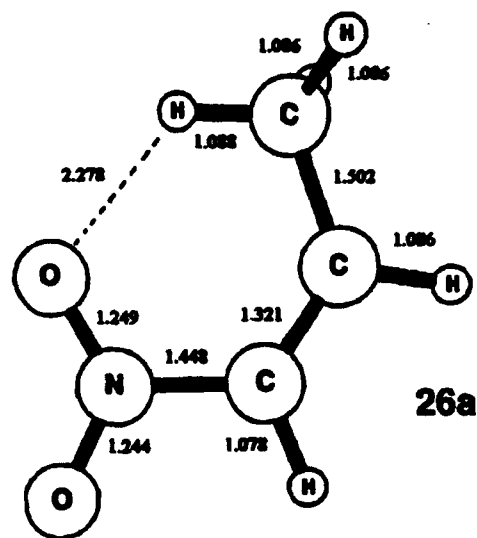


Figure 8. MP2/6-31G* Structures of the cis Tautomers of 1-Nitropropene and their Transition Structure.

TABLE 8. ABSOLUTE ENERGIES (in - hartrees) OF SUBSTITUTED NITROETHYLENE TAUTOMERS AND THEIR ANIONS.^a

Compound		HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G ^{ab}
C₂H₃NO₂					
16	C _s	354.34455 (0)	356.37129 (0)	357.36069 (0)	357.398291
16a	C _s	354.31813 (0)	356.35286 (0)	357.34116 (0)	357.34189
17	C _s	354.33883 (0)	356.35703 (0)	357.35329 (0)	357.38967
18	C _s	354.33310 (1)	356.34804 (1)	357.34911 (1)	357.38392
19	C ₁	354.33225 (0)	356.37765 (0)	357.36617 (0)	357.40566
20	C _s	353.78110 (0)	355.81821 (0)	356.80925 (0)	356.84379
C₂H₄N₂O₂					
21	C _s	334.63553 (0)	336.54755 (0)	337.52181 (0)	337.56267
22	C _s	334.61206 (0)	336.51574 (0)	337.49950 (0)	337.53963
23	C _s	334.61017 (1)	336.50763 (1)	337.49748 (1)	337.53609
24	C ₁	334.60560 (0)	336.54003 (0)	337.51459 (0)	337.55875
25	C _s	334.02769 (0)	335.95711 (0)	336.93604 (0)	336.97493
C₃H₃NO₂					
26	C _s	318.71225 (0)	320.54169 (0)	321.48544 (0)	321.53231
26a	C _s	318.71184 (0)	320.54120 (1)	321.48438 (1)	321.53118
27	C ₁	318.71557 (0)	320.51239 (0)	321.45489 (0)	321.50247
28	C ₁	318.64118 (1)	320.44925 (1)	321.41821 (1)	321.45982
29	C ₁	318.70877 (0)	320.54121 (0)	321.48403 (0)	321.53107
30	C _s	318.13774 (0)	319.95544 (0)	320.90327 (0)	320.94546

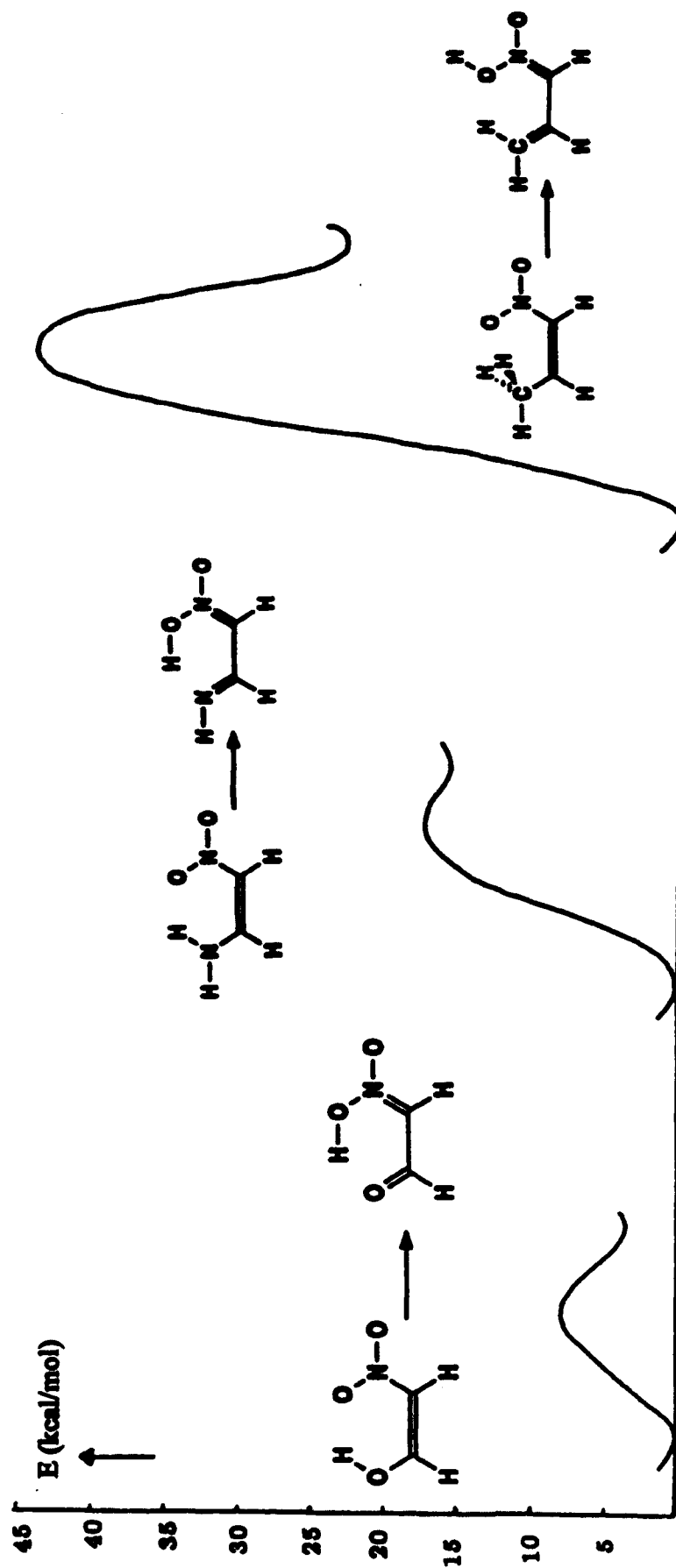
^a Values in parentheses are the number of imaginary frequencies. ^b MP2/6-31G* geometries.

TABLE 9. RELATIVE ENERGIES (in kcal/mol) OF SUBSTITUTED NITROETHYLENE TAUTOMERS AND THEIR ANIONS.

Compound		HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G**	MP4/6-31G** + ZPE
<u>C₂H₃NO₂</u>						
16	C _s	0.0	0.0	0.0	0.0	0.0
16a	C _s	16.6	11.6	12.3	12.0	12.4
17	C _s	3.6	8.9	4.7	5.4	4.8
18	C _s	7.2	14.0	7.3	9.0	5.8
19	C ₁	7.7	-4.0	-3.4	-4.6	-3.6
20	C _s	353.6	347.1	346.0	348.0	339.1
<u>C₂H₄N₂O₂</u>						
21	C _s	0.0	0.0	0.0	0.0	0.0
22	C _s	14.7	19.9	14.0	14.5	14.5
23	C _s	15.9	25.1	15.3	16.7	13.9
24	C ₁	18.8	4.7	4.5	2.5	2.4
25	C _s	381.4	370.5	367.6	368.8	360.4
<u>C₃H₅NO₂</u>						
26	C _s	0.0	0.0	0.0	0.0	0.0
26a	C _s	0.3	0.3	0.7	0.7	0.6
27	C ₁	-2.1	18.4	19.2	18.7	18.7
28	C ₁	44.6	58.0	42.2	45.5	42.4
29	C ₁	2.2	0.3	0.9	0.8	1.1
30	C _s	360.5	367.8	365.3	368.3	360.0

* MP2/6-31G* geometries.

Energies of Substituted Nitroethylene Tautomers



	Nitro	TS	aci-Nitro	Nitro	TS	aci-Nitro	Nitro	TS	aci-Nitro
HF/3-21G	0.0	7.2	3.6	0.0	15.9	14.7	0.0	44.6	-2.1
HF/6-31G*	0.0	14.6	8.9	0.0	25.1	19.9	0.0	58.0	18.4
MP2/6-31G*	0.0	7.3	4.7	0.0	15.3	14.0	0.0	42.2	19.2

Figure 9. Energy Profile of Substituted Nitroethylene Tautomers. The Graph Displays MP2/6-31G* Energies.

TAUTOMERISM IN CONJUGATED NITRO COMPOUNDS

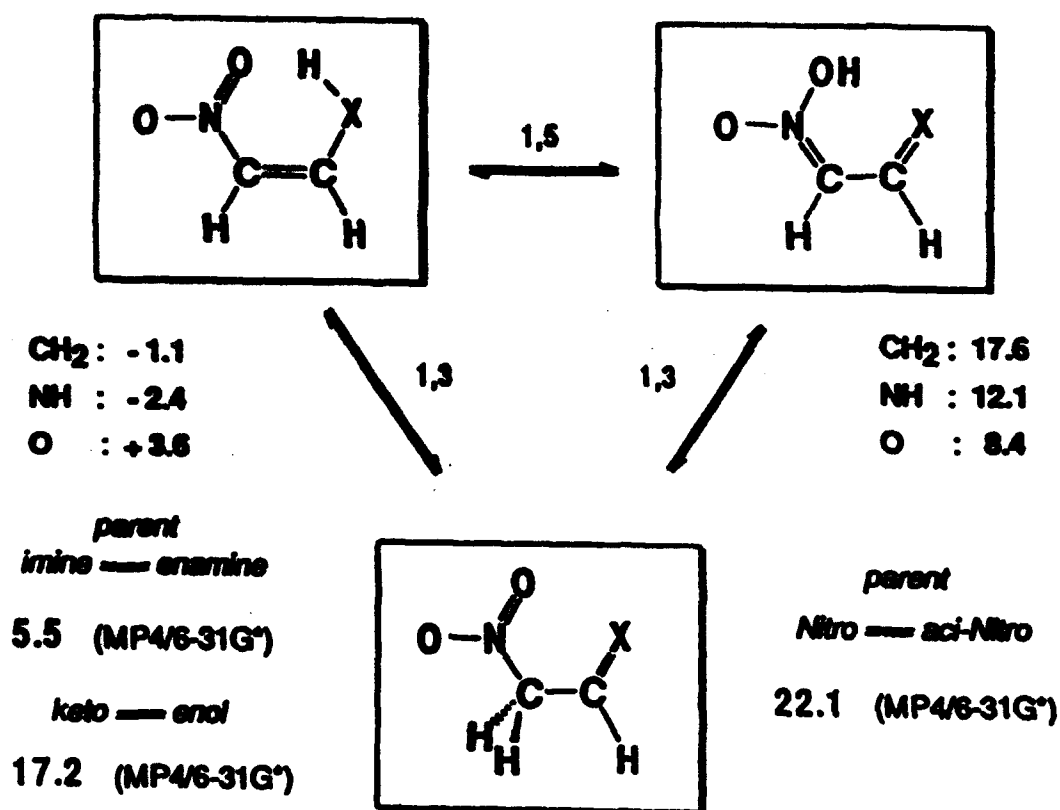
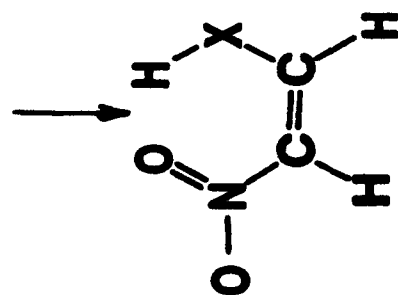
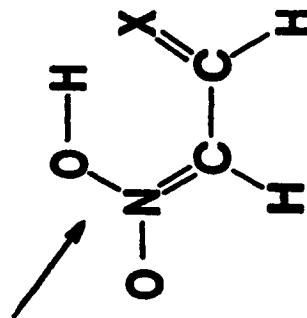


Figure 10. MP4/6-31G* Energy Comparisons (in kcal/mol) between Substituted Nitroethylenes Tautomers and the Parent Nitro/*aci*-Nitro, Keto/Enol, and Imine/Enamine Tautomers.



X = O
 = NH
 = CH₂



Bond Critical Point Data for Substituted Nitroethylenes.

Compound	$\rho(r)$	$\nabla^2 \rho(r)$	$H(r)$
<u>Hydrogen Bond</u>			
HO-CH=CH-NO ₂	0.263	3.386	-0.008
H ₂ N-CH=CH-NO ₂	0.184	2.306	-0.003
H ₂ C-CH=CH-NO ₂	0.100	1.417	0.008

Bond Critical Point Data for aci-Nitroethylenes.

Compound	$\rho(r)$	$\nabla^2 \rho(r)$	$H(r)$
<u>N(1)-O(5)H</u>			
O=CH-CH=NO ₂ H	2.474	-17.689	-2.605
HN=CH-CH=NO ₂ H	2.334	-10.881	-2.363
H ₂ C=CH-CH=NO ₂ H	2.112	-8.359	-1.992

Figure 11. Hydrogen Bonding at MP2/6-31G* for Substituted Nitroethylenes and N-OH Bond Strengths in their aci-Nitro Tautomers.

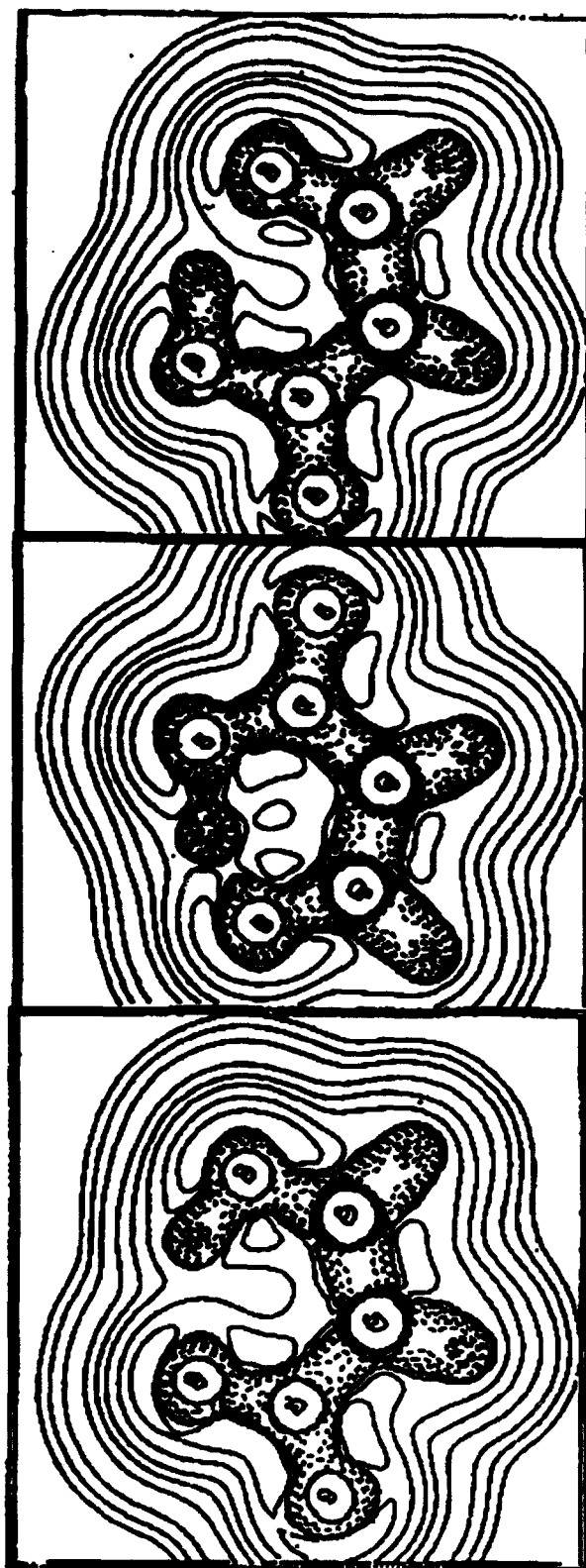


Figure 12. Relief Map of the Total Electron Density (Top) and the Laplacian (Bottom) of 2-Nitrovinyl Alcohol (Left), its Nitronic Acid (Right), and the Transition Structure (Middle).

SECTION IV

TAUTOMERISM IN SUBSTITUTED NITROBENZENES

1. INTRODUCTION

We consider *o*-nitrophenol, *o*-nitroaniline, and *o*-nitrotoluene in this section. Their HF/3-21G and HF/6-31G* optimized structures and those of their *aci*-tautomers and the transition structures for 1,5-H shifts are displayed in Figures 13-15. Total HF and MP/6-31G* and relative energies are given in Table 10, and visualized in Figures 16 and 17.

2. BACKGROUND

The study by Politzer and coworkers on the tautomerism of *o*-nitrophenol (Reference 1), and their data on this tautomeric pair, and their unsuccessful attempts of finding tautomerism in other substituted nitroaromatic compounds⁴⁴ form the underpinnings of this investigation. Of particular interest are the reported tautomer of *o*-nitrophenol and the author's inability to locate similar tautomeric structures for *o*-nitroaniline and *o*-nitrotoluene. These calculations were performed at the 3-21G level of theory and the results are counterintuitive to those in the previous section. It is important to stress that the conformation of *aci*-2-nitrophenol, reported by the Politzer group, has a syn orientation of the (O)NO—H bond with respect to the neighboring C=O group with an energy difference of 15.4 kcal/mol between the two tautomers.

3. DISCUSSION

The HF/6-31G* optimized structures of the nitro compounds are in reasonable agreement with X-ray structures (Reference 42). The largest differences are found for the C—N and N—O bonds as already discussed in Section II. The (O)NO...HO distance in *o*-nitrophenol is relatively short with 1.826 Å at HF/6-31G* (1.91 Å, X-ray; 1.748 Å, HF/3-21G) and this is also the case for the (O)NO...HNH distance in *o*-nitroaniline for which the HF/6-31G* separation is calculated at 1.991 Å (1.955 Å, X-ray). However, numerous attempts to calculate the nitronic acid tautomer of both *o*-nitrophenol, (as reported by Politzer and coworkers), and *o*-nitroaniline at HF/3-21G proved unsuccessful. These tautomers could only be calculated with the larger 6-31G* basis set at which level also the transition structures were determined and characterized. However, the kinetic stability of both nitronic acids is less than 1 kcal/mol. Single point calculations that include the effects of electron correlation at MP2/6-31G* give lower relative energies for the transition structures than for the nitronic acid tautomers. This is illustrated in Figure 17 and strongly suggests that the nitronic acid tautomers of *o*-nitrophenol and *o*-nitroaniline are not likely to have a trans *aci*-nitro conformation. In this context it is relevant to recall that the *aci*-nitro tautomer of 1-nitropropene has a cis conformation of the (O)NO—H group.

Optimization of the nitronic acids of *o*-nitrophenol, *o*-nitroaniline, and *o*-nitrotoluene with a *cis* orientation within the O←N—O—H *aci*-nitro group results in local minima in all cases. The transition structures for the [1,5]-H shift were also identified and the results are displayed in Figure 17. Three observations can be made. Firstly, the nitronic acids have significant kinetic stabilities, i.e. 14.0 kcal/mol for *o*-nitrophenol, 4.2 kcal/mol for *o*-nitroaniline, and 6.2 kcal/mol for *o*-nitrotoluene (MP2/6-31G* + ZPE). Secondly, the energy differences (same level) between the tautomers increase from *o*-nitrophenol (30.7 kcal/mol) to *o*-nitroaniline (43.3 kcal/mol) to *o*-nitrotoluene (46.3 kcal/mol). Thirdly, these kinetic and thermodynamic energy differences are much larger than those of the substituted nitroethylenes (except for nitropropylene) and those of the O←N—O—H *trans* conformations of the aromatic nitronic acids. The influence of electron correlation (at MP2) on the energies is only modest except for the rearrangement barrier of *o*-nitrotoluene. It must be emphasized that whereas all nitro compounds show small distortions from planarity at HF/6-31G* the transition structures deviate significantly from planarity, both for the transferring H and for the aromatic ring. This is illustrated in Figures 13-16. The main conclusion from this section is that nitro ⇌ *aci*-nitro tautomerism is feasible for *o*-substituted nitrobenzenes only when the nitronic acid has a *cis* O←N—O—H conformation.

Nitro \rightarrow aci-Nitro Tautomerism in ortho-Nitrophenol

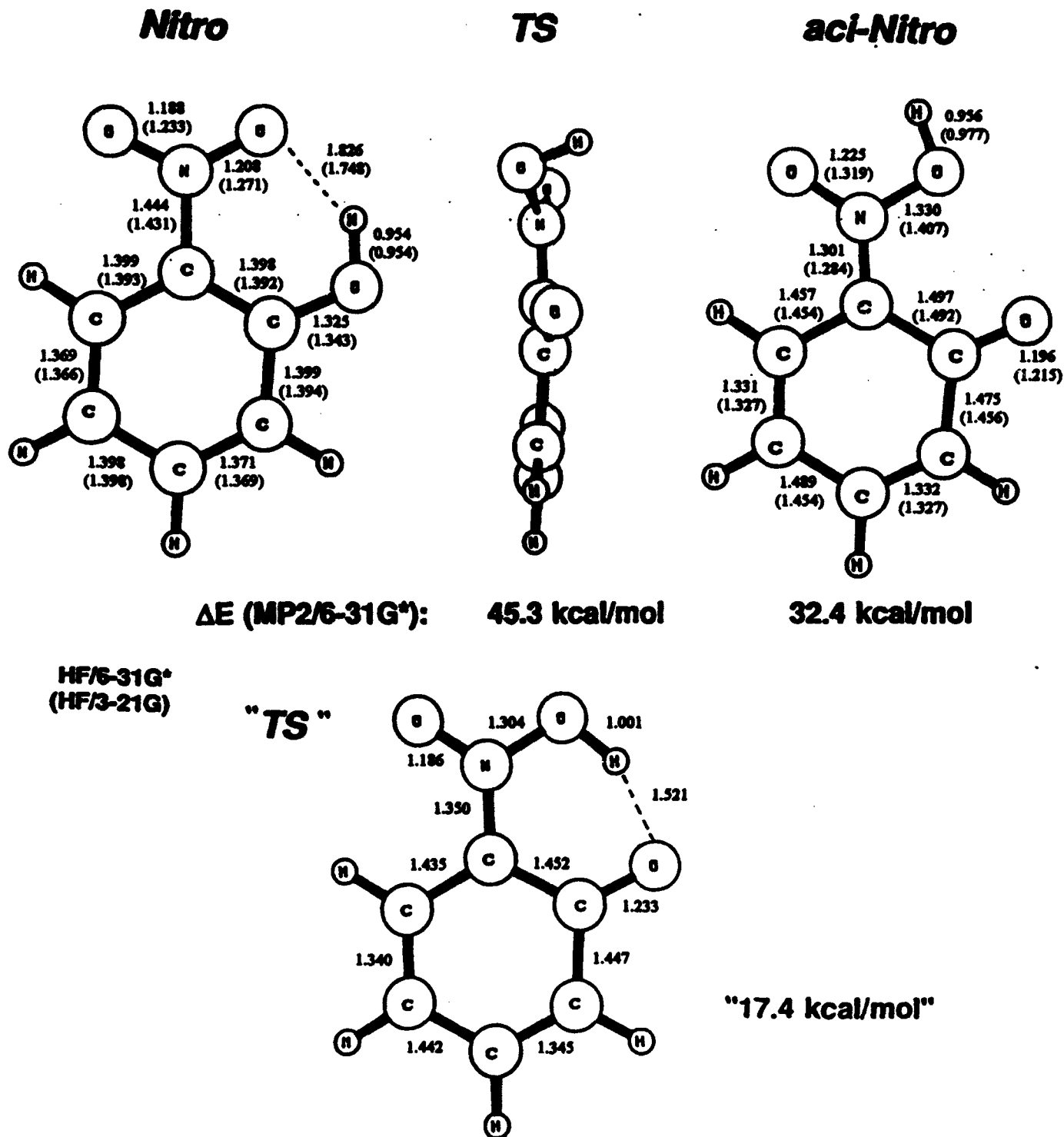


Figure 13. Tautomers of *o*-Nitrophenol.

Nitro \rightarrow aci-Nitro Tautomerism in ortho-Nitroaniline

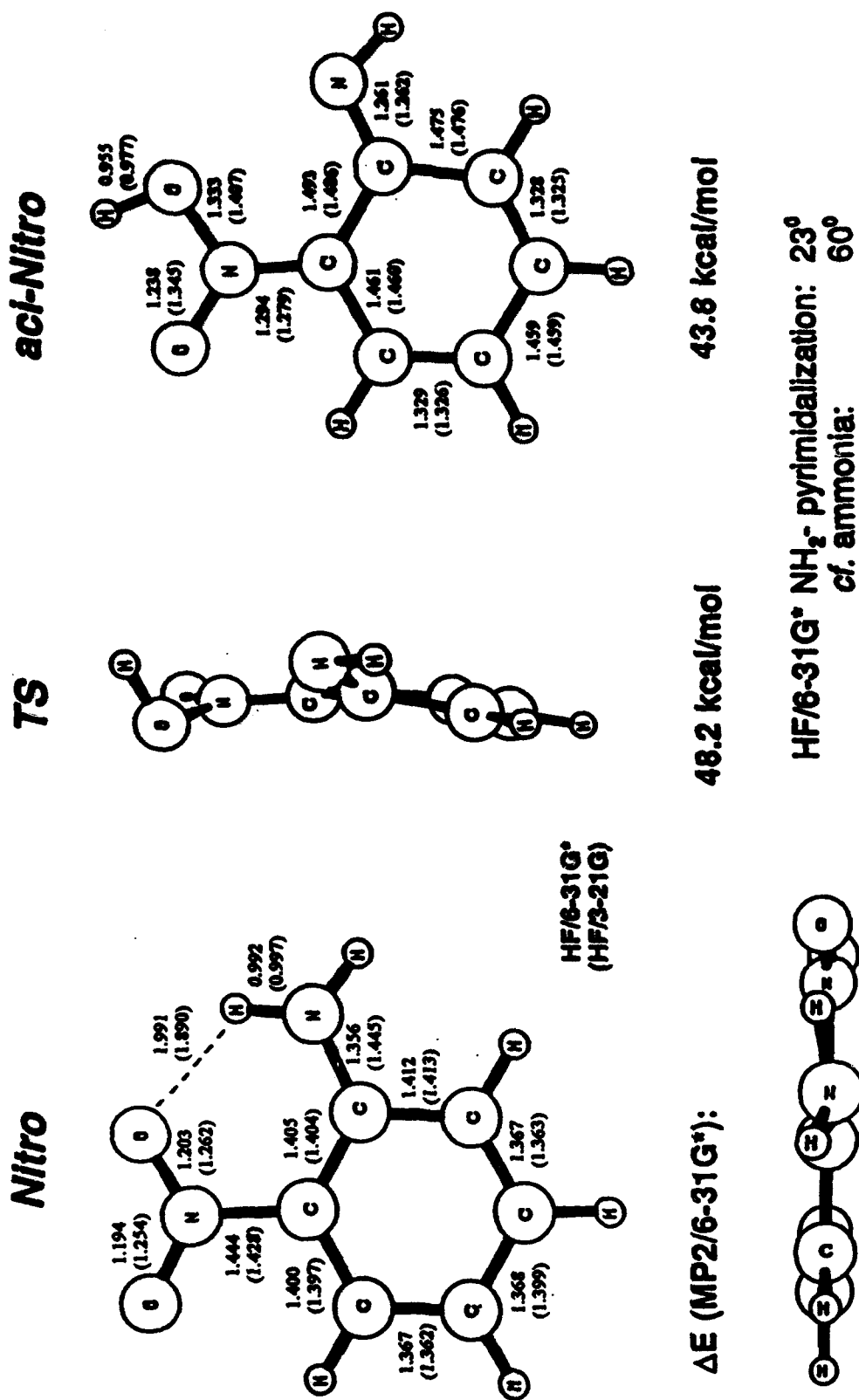


Figure 14. Tautomers of o-Nitroaniline.

Nitro \leftrightarrow *aci*-Nitro Tautomerism in *ortho*-Nitrotoluene

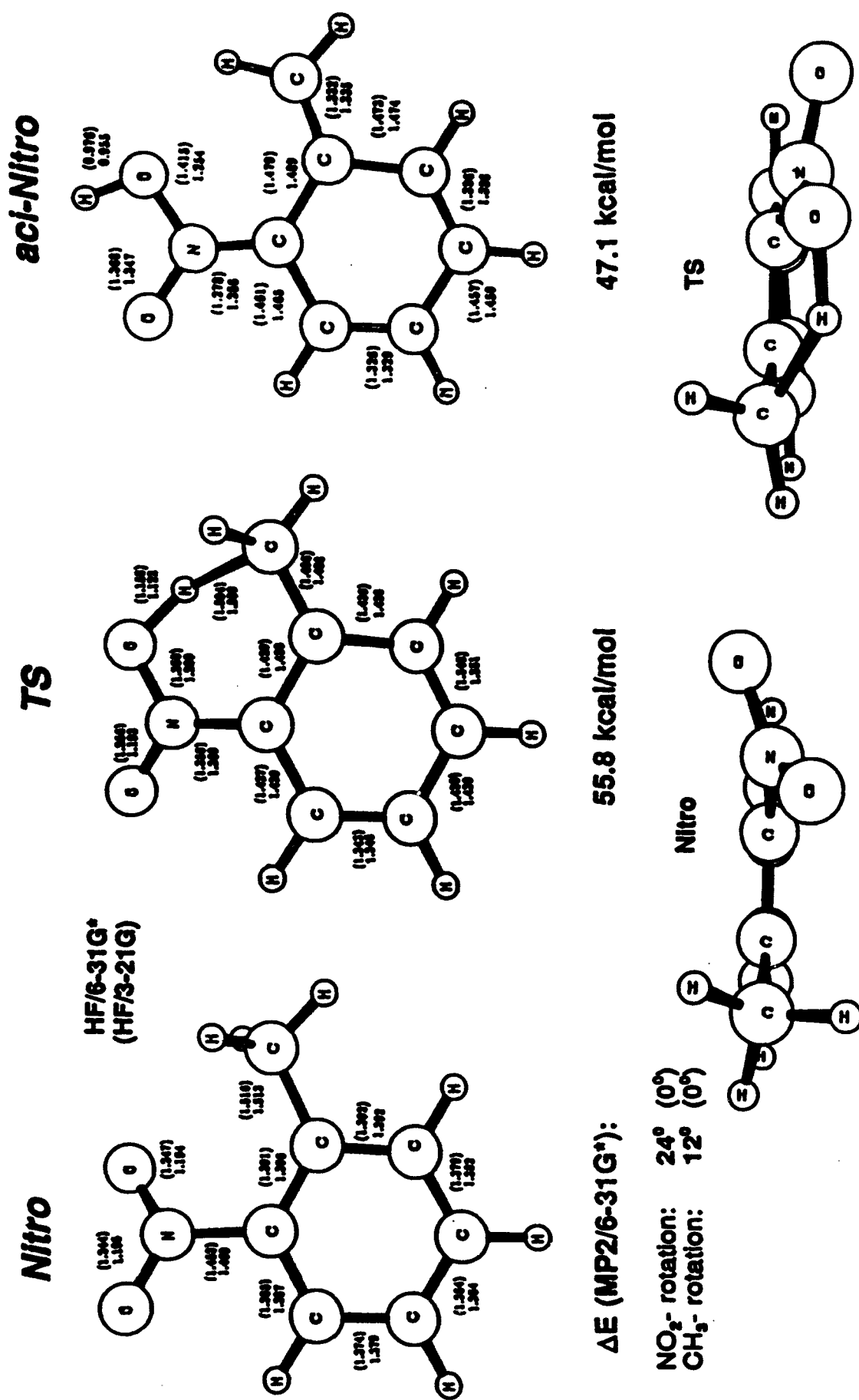


Figure 15. Tautomers of *o*-Nitrotoluene.

TABLE 10. TOTAL (in - hartrees) AND RELATIVE (in kcal/mol) ENERGIES OF ortho-SUBSTITUTED NITROBENZENES.

Compound	Symm	<u>HF/3-21G</u>		<u>HF/6-31G*</u>		<u>MP2/6-31G*</u>		(+ZPE)
		abs.	rel.	abs.	rel.	abs.	rel.	rel. (corr.)
<u><i>o</i>-Nitrophenol</u>								
Nitro	C _s	506.16267	0.0 (0)	509.03467	0.0 (0)	510.53947	0.0	0.0
<i>aci</i> -Nitro	C _s	506.12296	24.9 (0)	508.98473	31.3 (0)	510.48805	32.4	30.7
TS	C _i	506.11313	31.1 (1)	508.96137	46.3 (1)	510.46729	45.3	44.7
" <i>aci</i> -Nitro"	C _s			509.00070	21.3 (0)	510.51178	17.4	20.4
"TS"	C _i			509.00026	21.6 (1)	510.51389	16.1	19.0
<u><i>o</i>-Nitroaniline</u>								
Nitro	C _i			489.20481	0.0 (0)	490.69636	0.0	0.0
	C _s	486.44531	0.0 (0)	489.20471	0.6 (1)	490.69587	0.3	0.2
<i>aci</i> -Nitro	C _s	486.38433	38.3 (0)	489.13598	43.3 (0)	490.62651	43.8	43.3
TS	C _i	486.37537	43.9 (1)	489.12801	48.2 (1)	490.61964	48.2	47.5
" <i>aci</i> -Nitro"	C _s			489.15236	32.9 (0)	490.65293	27.3	32.4
"TS"	C _i			489.15196	33.2 (1)	490.65536	25.7	32.2
<u><i>o</i>-Nitrotoluene</u>								
Nitro	C _i			473.20773	0.0 (0)	474.67211	0.0	0.0
	C _s	470.53030	0.0 (0)	473.20744	0.2 (1)	474.67136	0.5	0.2
<i>aci</i> -Nitro	C _s	470.49368	23.0 (0)	473.13890	43.2 (0)	474.59710	47.1	46.3
TS	C _i	470.43853	57.6 (1)	473.09709	69.4 (1)	474.58319	55.8	52.5

Energies of Substituted Nitroaromatic Tautomers

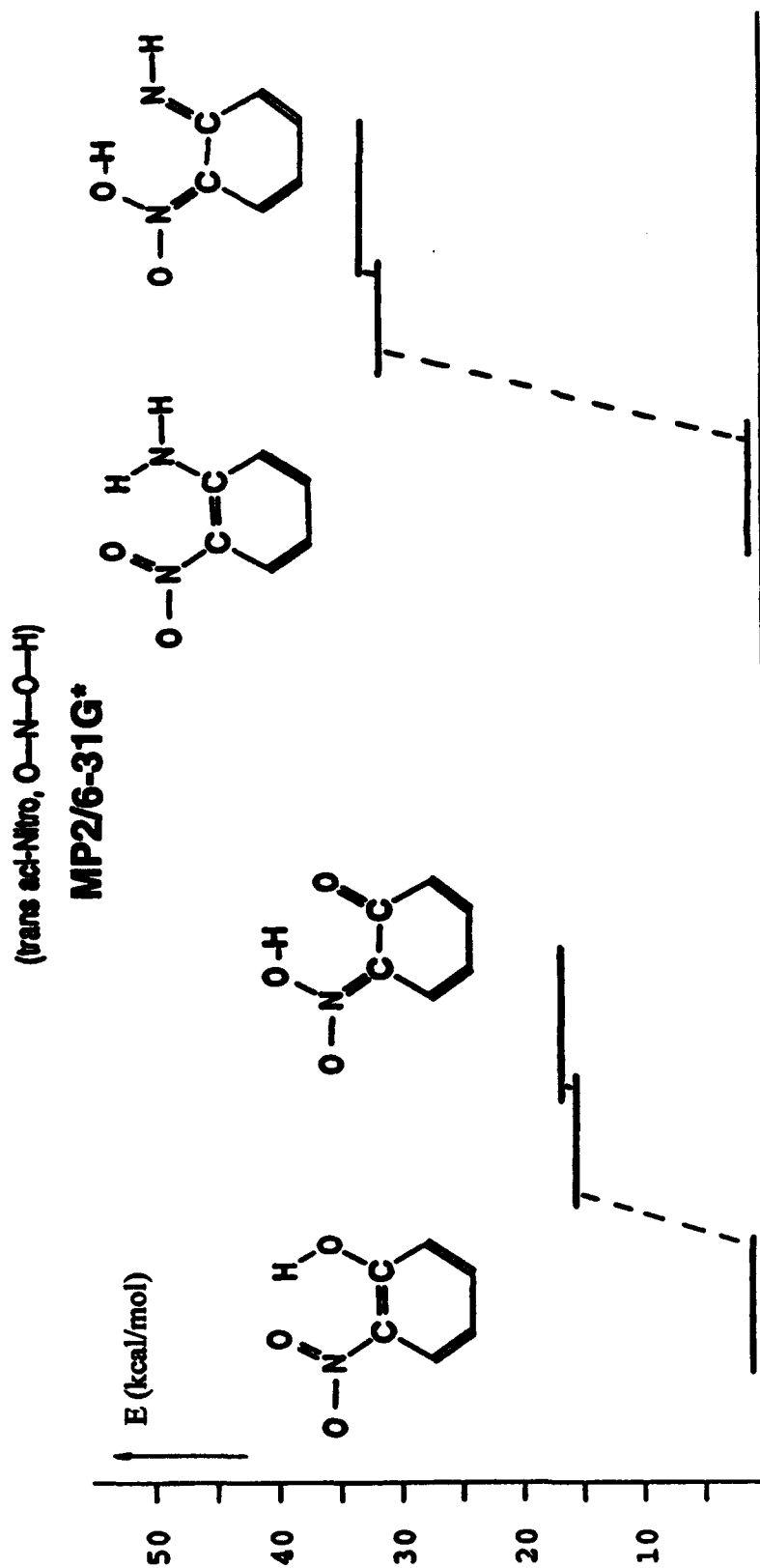
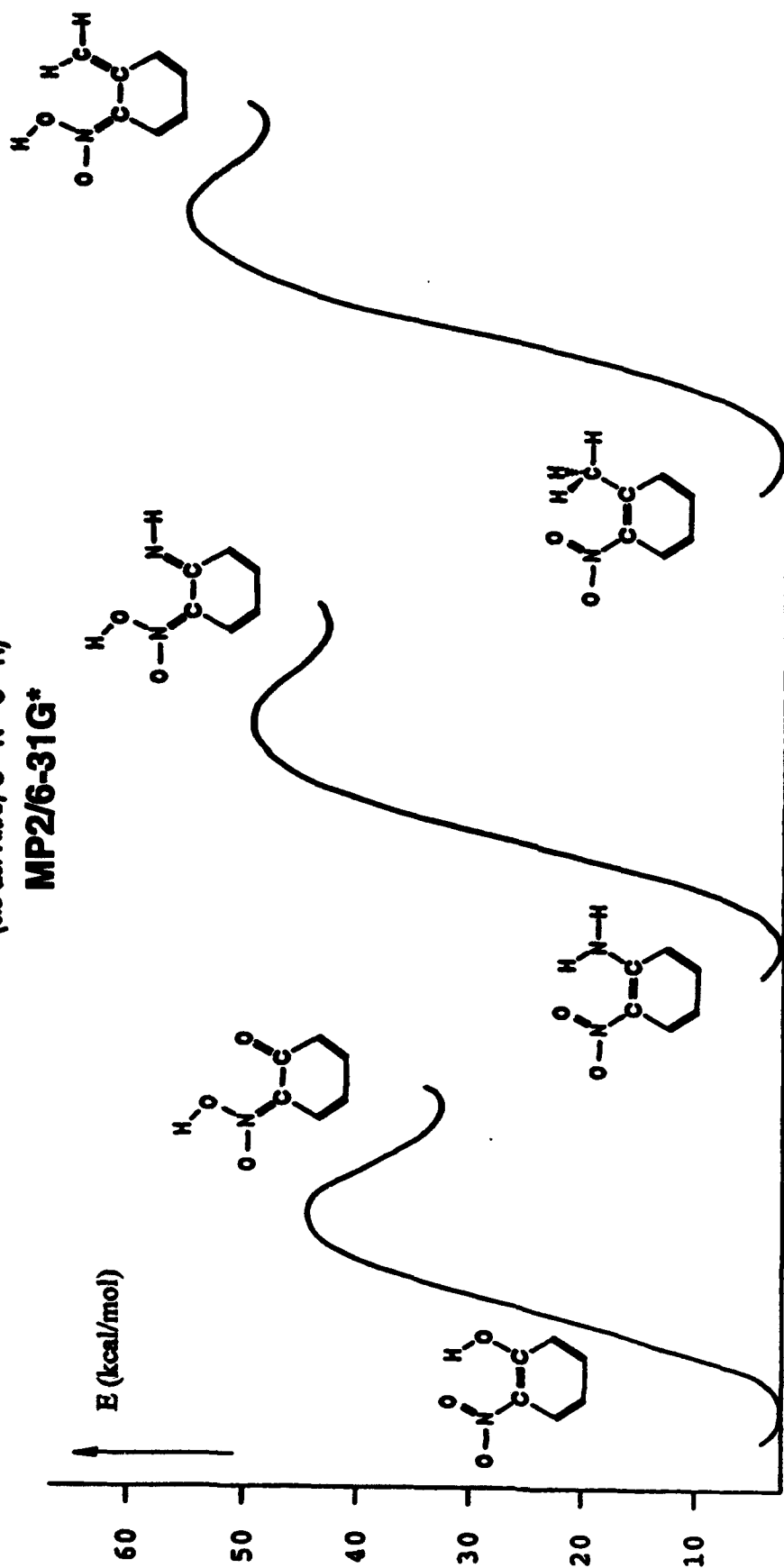


Figure 16. Energy Profile of Tautomerism of *o*-Nitrophenol and *o*-Nitroaniline to trans Nitronic Acids.

Energies of Substituted Nitroaromatic Tautomers

(cis aci-Nitro, O—N—O—H)

MP2/6-31G*



	<u>Nitro</u>	<u>TS</u>	<u>aci-Nitro</u>	<u>Nitro</u>	<u>TS</u>	<u>aci-Nitro</u>
HF/3-21G	0.0	31.1	24.9	0.0	43.9	38.3
HF/6-31G*	0.0	46.0	31.3	0.0	48.2	43.3
MP2/6-31G*	0.0	45.3	32.4	0.0	48.2	43.8
				0.0	57.6	23.0
				0.0	69.4	43.2
				0.0	55.8	47.1

Figure 17. Energy Profile of Tautomers of *ortho*-Substituted Nitrobenzenes.

SECTION V

TAUTOMERISM IN SUBSTITUTED DINITROBENZENES

1. INTRODUCTION

We consider 2,6-dinitrophenol, 2,6-dinitroaniline, and 2,6-dinitrotoluene. The HF/3-21G and HF/6-31G* optimized parameters of the nitro, *aci*-nitro, and related transition structures are shown in Figures 18-20. Total and relative 3-21G and 6-31G* energies are given in Table 11

2. DISCUSSION

Many of the same observations as those discussed in the section on substituted nitrobenzenes also apply to the dinitrobenzenes. However, the buttressing effect of the second nitro group is evident and this affects the three nitro compounds in different ways. One nitro group is significantly rotated (37°) in 2,6-dinitrophenol, both nitro groups are planar in the aniline derivative due to H-bonding ((O)NO...HNH = 1.959 Å), while both nitro groups are rotated (35°) in the toluene derivative to minimize the repulsion with the methyl group. The same applies to the nitronic acids with NO₂ bond rotations of 35° for the dinitrophenol tautomer and 23° for the dinitrotoluene tautomer, and the dinitroaniline tautomer is now also non-planar. All tautomers are minima. The transition structures for the [1,5]-H transfer were also characterized at both HF/3-21G and HF/6-31G*. Comparison of the HF/6-31G* energy differences (ΔE) between the nitro - *aci*-nitro tautomeric pairs, (barriers are in parentheses), with those of the mononitro species highlight subtle but important differences. For example, ΔE for 2,6-dinitrophenol is 29 (34) kcal/mol whereas a much larger barrier of 46 kcal/mol ($\Delta E = 31$) is calculated for *o*-nitrophenol. The 2,6-dinitro derivative of aniline has a much larger ΔE of 45 (49) kcal/mol than that of phenol, but in contrast it compares with the 43 (48) kcal/mol calculated for *o*-nitroaniline. The aniline nitro \rightleftharpoons *aci*-nitro energy differences, but not the barriers, are comparable in magnitude to the 41 (65) kcal/mol for 2,6-dinitrotoluene and the 43 (69) kcal/mol for *o*-nitrotoluene. The effects of electron correlation in the ΔE values could not be evaluated directly due to limitations in resources. However, if the influence of electron correlation (MP2) on ΔE for the dinitro derivatives is similar to that for the mononitro compounds, then it must be assumed that the barrier for [1,5]-H transfer will reduce significantly at correlated levels. Nevertheless, it appears that the tautomeric ΔE is slightly less for dinitrotoluene than it is for dinitroaniline.

Tautomers of 2,6-Dinitrophenol

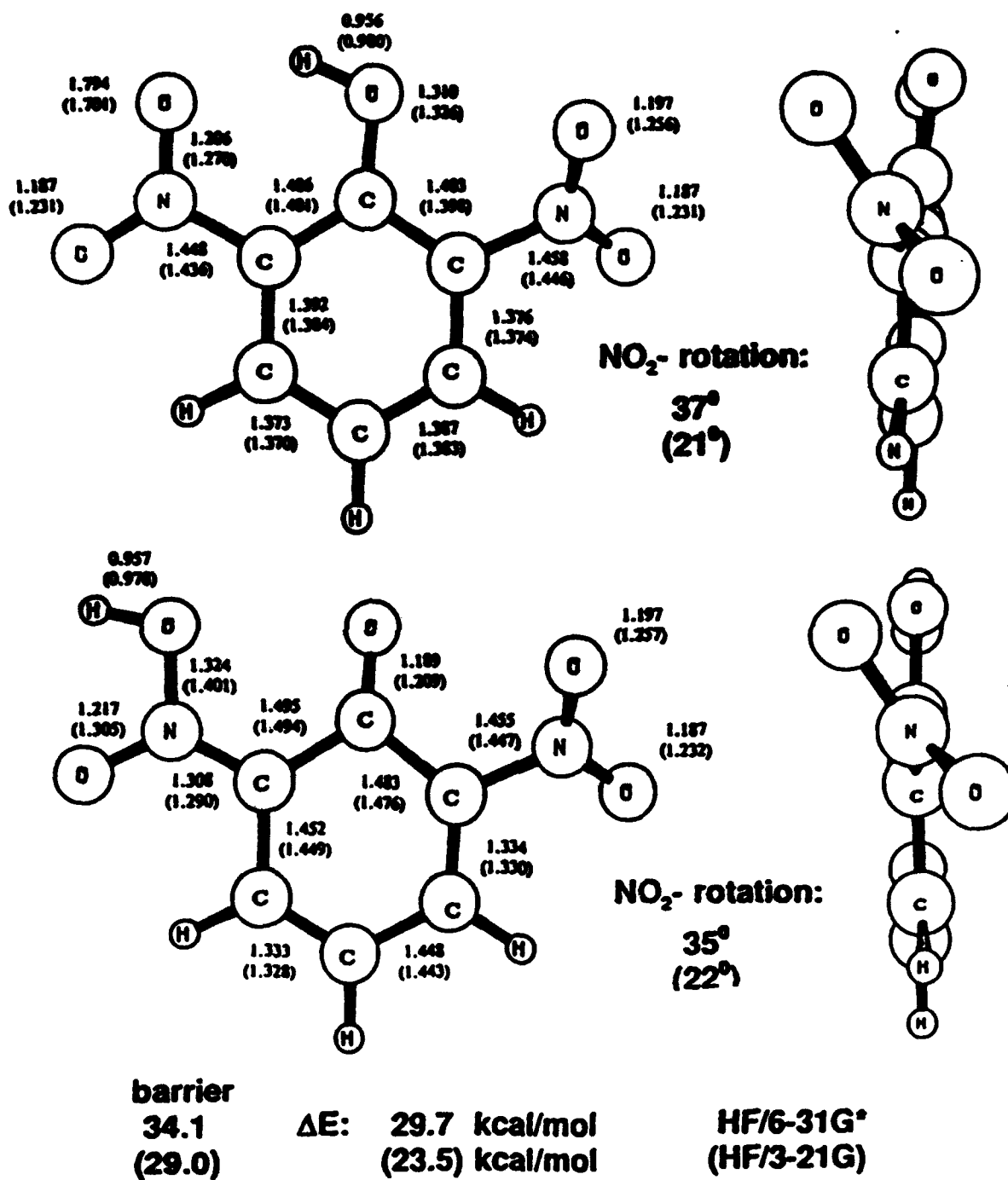


Figure 18. Optimized Tautomeric Structures of 2,6-Dinitrophenol:

Tautomers of 2,6-Dinitroaniline

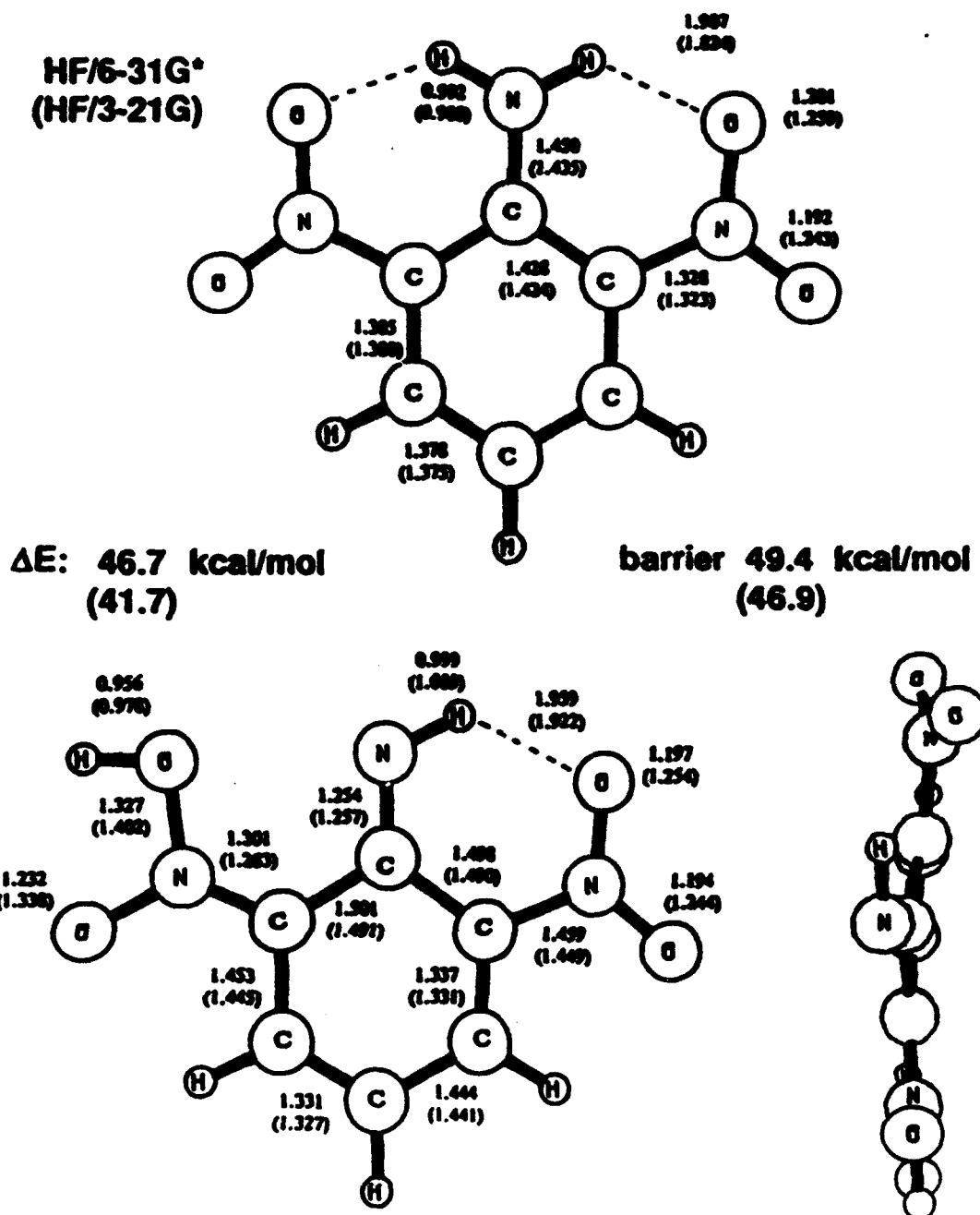


Figure 19. Optimized Tautomeric Structures of 2,6-Dinitroaniline.

Tautomers of 2,6-Dinitrotoluene

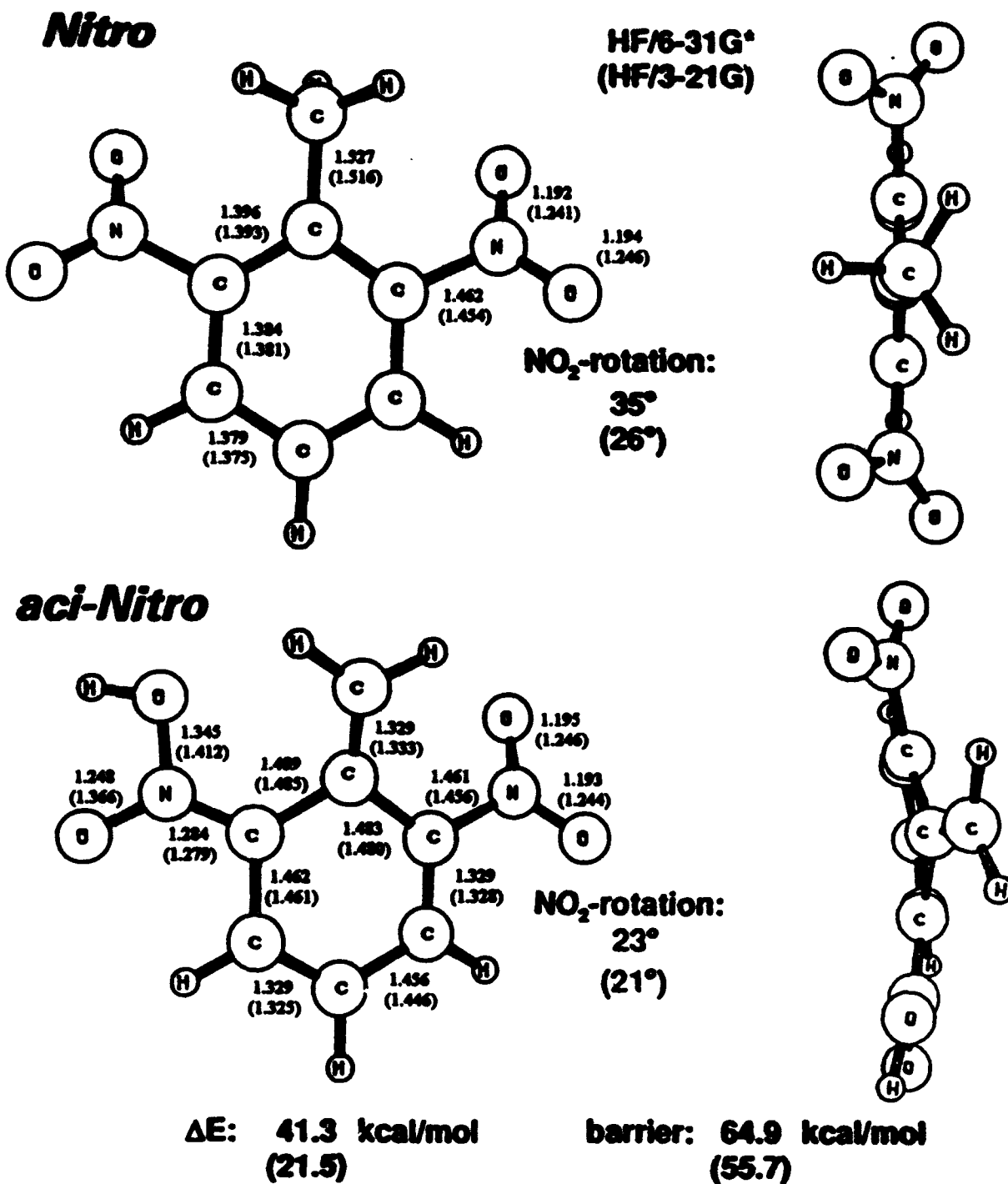


Figure 20. Optimized Tautomeric Structures of 2,6-Dinitrotoluene.

TABLE 11. TOTAL (in - hartrees) AND RELATIVE (in kcal/mol) ENERGIES OF SUBSTITUTED DINITROBENZENES.

Compound	Symm.	<u>HF/3-21G</u>		<u>HF/6-31G*</u>		rel.	<u>(+ZPE)</u>
		abs.	rel.	abs.	rel.		
<u>2,6-dinitrophenol</u>							
Nitro	C ₁	708.43505	0.0 (0)	712.48815	0.0 (0)	0.0	0.0
<i>aci</i> -Nitro	C ₁	708.38760	23.5 (0)	712.44084	29.7 (0)	29.2	29.2
TS	C ₁	708.38882	29.0 (1)	712.43194	35.3 (1)	34.1	34.1
<u>2,6-dinitroaniline</u>							
Nitro	C ₁	688.73738	0.0 (0)	692.67099	0.0 (0)	0.0	0.0
<i>aci</i> -Nitro	C ₁	688.67100	41.7 (0)	692.59710	46.4 (0)	46.1	46.1
TS	C ₁	688.66271	46.9 (1)	692.59079	50.3 (1)	49.4	49.4
<u>2,6-dinitrotoluene</u>							
Nitro	C ₁	672.80767	0.0 (0)	676.66474	0.0 (0)	0.0	0.0
<i>aci</i> -Nitro	C ₁	672.77344	21.5 (0)	676.59853	41.5 (0)	41.3	41.3
TS	C ₁	672.71889	55.7 (1)	676.55605	68.2 (1)	64.9	64.9

SECTION VI

TAUTOMERISM IN PICRIC ACID, PICRAMIDE, AND TNT

1. INTRODUCTION

In this section we consider picric acid, picramide, and TNT. Their fully optimized and characterized, non-symmetric nitro, *aci*-nitro, and corresponding transition structures are displayed in Figures 21-23. Total and relative HF/3-21G and HF/6-31G* energies are given in Table 12.

2. DISCUSSION

The optimized nitro compound structures compare well to those reported from X-ray structure determinations (Reference 43). As referred to in the previous sections, the largest discrepancies are with the N-O and C-N bonds but in these cases also deviations are found for the rotation of the nitro groups. As compared to the dinitro derivatives of the previous section, addition of the third nitro group has a subtle but important influence beyond that of a spectator at the 4-position. The geometrical parameters for picric acid and 2,6-dinitrophenol are very similar, even for the *o*-nitro group HF/6-31G* bond-rotations of 35° and 37°, respectively, with corresponding rotations of 38° and 35° for their nitronic acids. However, the two X-ray crystal structures of picric acid indicate a much smaller rotation of 'only' 17-20°, which interestingly compares well with the HF/3-21G value of 20°. Picramide has a planar structure which compares well the X-ray structure and is similar to that of 2,6-dinitroaniline. This suggests that it is also similarly stabilized by two H-bonds between the nitro groups and the amine group. TNT is non-planar but does have a plane of symmetry. Like 2,6-dinitrotoluene, its nitro groups are rotated (36°, 6-31G*; 43-51, exp.) with one of the oxygens of each nitro group bisecting the neighboring methyl group. This conformation is the same as for the mono- and dinitro derivatives. The nitronic acid tautomer of TNT has a 'benzene' ring that is significantly distorted from planarity. This is likely the result of steric congestion between the methylene group and its neighboring *aci*-nitro and nitro groups. The nitro group rotation is 25°.

The energy differences between the nitro compounds and their *aci*-nitro tautomers amplify the trend already observed for the dinitro compounds. Barriers for [1,5]-H transfer from the nitro to the nitronic acid tautomers are given in parentheses. Thus, ΔE (HF/6-31G*) for picric acid has reduced to 25 (34) from 29 (34) kcal/mol for dinitrophenol. Likewise, ΔE for TNT of 39 (65) kcal/mol is smaller than the 41 (65) kcal/mol for dinitrotoluene. In contrast, a larger ΔE of 48 (51) kcal/mol is calculated for picramide as compared to a ΔE of 45 (49) for dinitroaniline. Even though these changes are small and can be individually explained by shortcomings in the theoretical levels employed, they continue the trend already observed for the dinitro derivatives.

3. CORRELATION BETWEEN SENSITIVITIES AND TAUTOMERISM

Important links between impact and shock sensitivities and the accessibility of tautomerism may be explored even though the levels of theory used for these large systems are inadequate to make definitive conclusions. Firstly, the energy difference between the tautomers of picric acid (25 kcal/mol, HF/6-31G*) as well as the barrier linking them (34 kcal/mol) is by far the smallest of the set of nitroaromatics studied. Picric acid is also the most sensitive compound. The calculated relative energy differences of both the nitronic acid and the transition structure are expected to be reduced further by the effects of electron correlation beyond MP2. Secondly, the energy difference between the tautomers of picramide (48 kcal/mol, HF/6-31G*) is somewhat larger than that between the TNT tautomers (39 kcal/mol). Picramide is also a less sensitive compound than TNT. Both picramide and TNT have significant barriers for tautomerism (51 and 65 kcal/mol, respectively, HF/6-31G*), but these are expected to reduce somewhat when the effects of electron correlation are taken into account with the larger effect expected for TNT. Thirdly, when the MP2/6-31G* reduction in the barrier for [1,5]-H transfer for *o*-nitrotoluene is applied to TNT, an activation barrier of 52 kcal/mol is estimated. This barrier is very similar to the experimental induction activation energy for thermal decomposition of liquid TNT. Fourthly, the tautomerism barriers for picramide and TNT are significantly higher than that of picric acid and may suggest alternative decomposition pathways for which there is experimental support.

Tautomers of Picric Acid

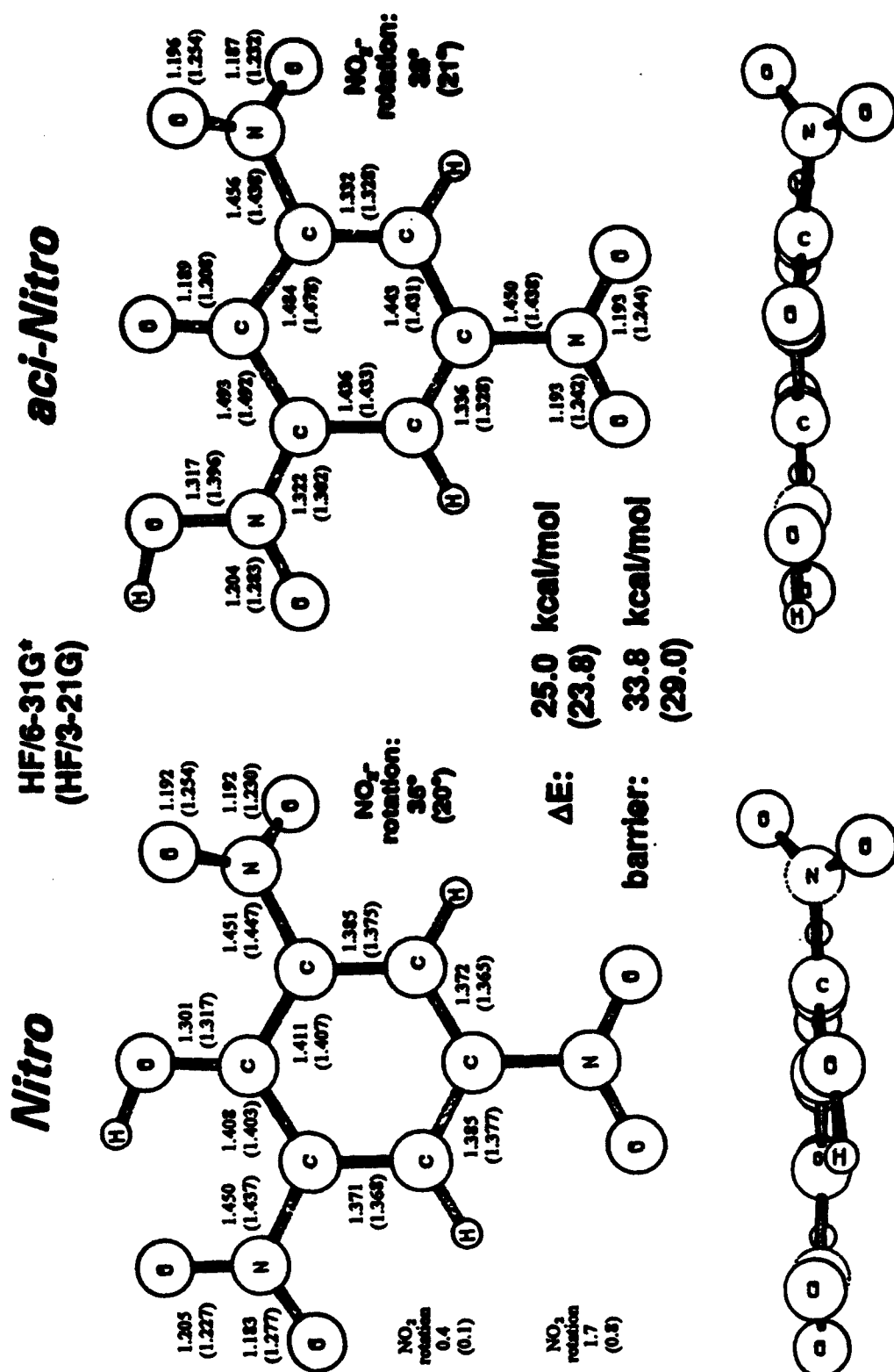


Figure 21. Optimized Tautomeric Structures of Picric Acid.

Tautomers of Picramide

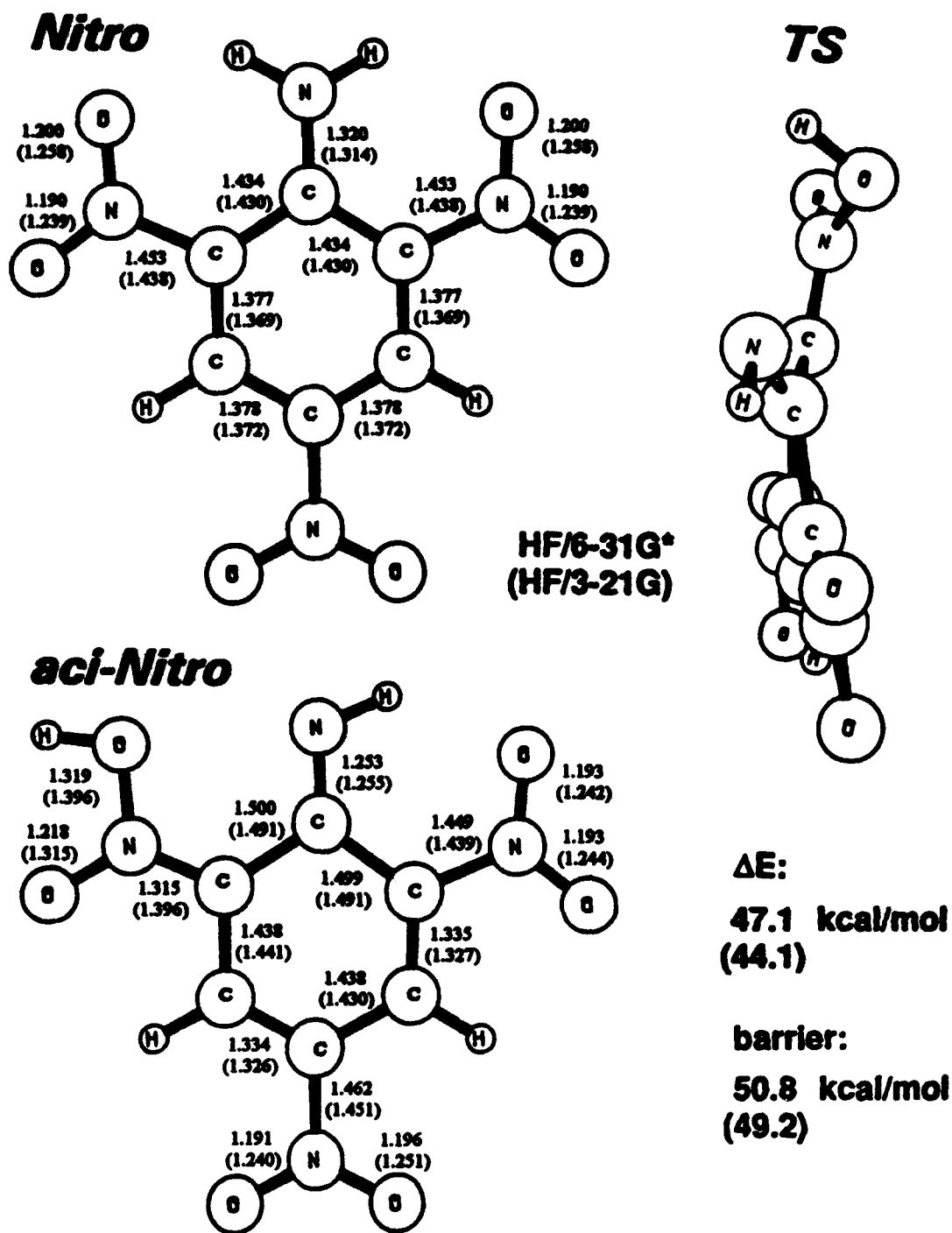
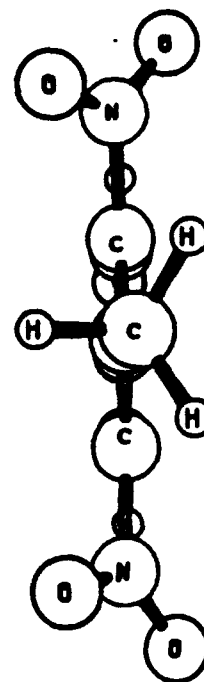
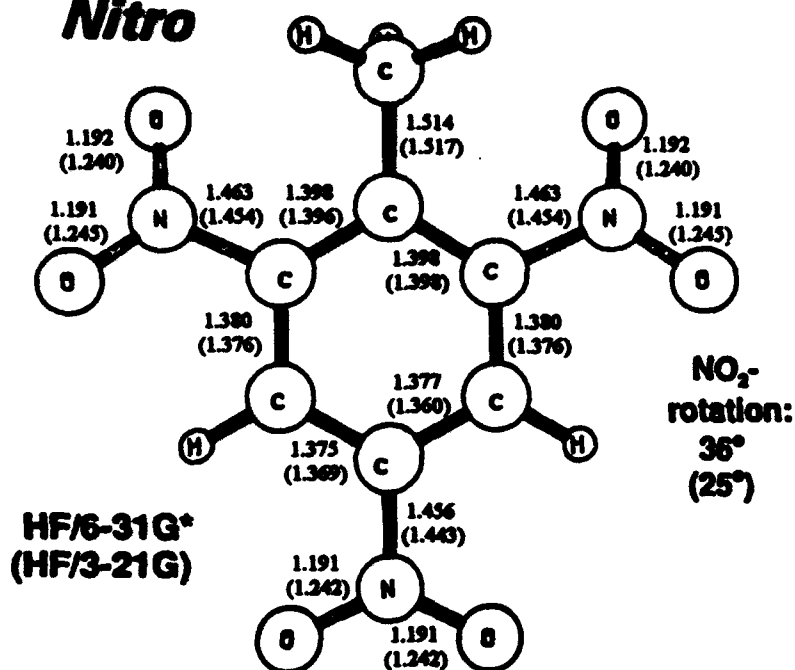


Figure 22. Optimized Tautomeric Structures of Picricamide.

Tautomers of TNT

Nitro



aci-Nitro

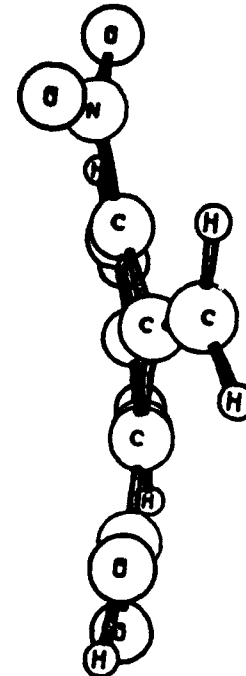
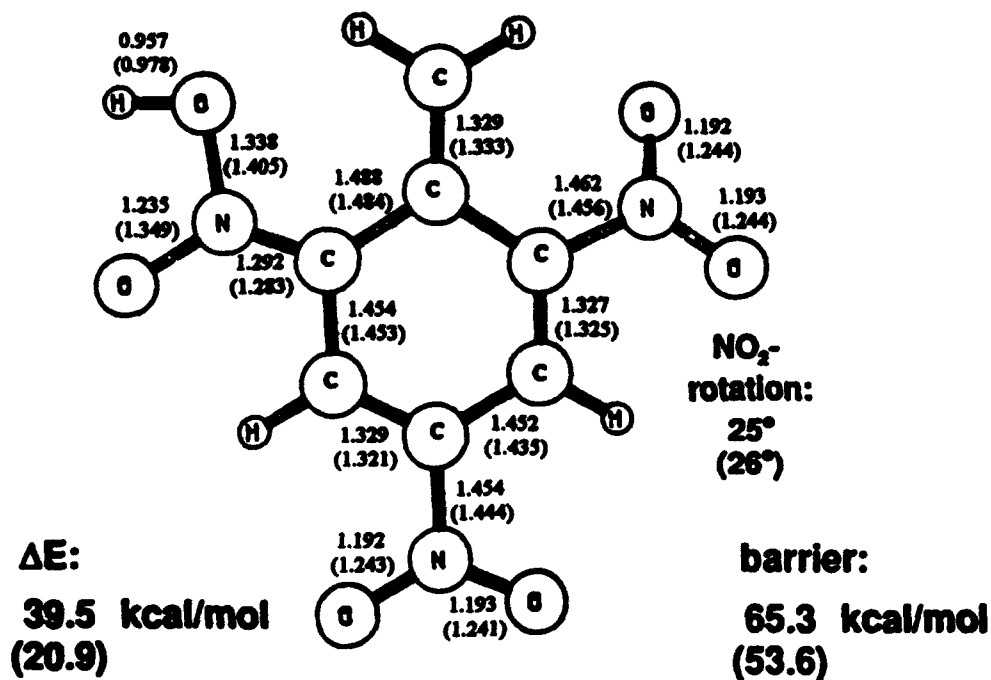


Figure 23. Optimized Tautomeric Structures of TNT.

TABLE 12. TOTAL (in - hartrees) AND RELATIVE (in kcal/mol) ENERGIES OF SUBSTITUTED TRINITROBENZENES.

Compound	Symm.	HF/3-21G		HF/6-31G*		rel.	rel.	(+ZPE)
		abs.	rel.	abs.	rel.			
2,4,6-trinitrophenol								
Nitro	C ₁	910.71661	0.0 (0)	915.94982	0.0 (0)			0.0
<i>aci</i> -Nitro	C ₁	910.67865	23.8 (0)	915.90354	29.0 (0)			25.0
TS	C ₁	910.67027	29.1 (1)	915.89403	35.0 (1)			33.8
2,4,6-trinitroaniline								
Nitro	C ₁	891.02344	0.0 (0)	896.13636	0.0 (0)			0.0
<i>aci</i> -Nitro	C ₁	890.95311	44.1 (0)	896.06064	47.5 (0)			47.1
TS	C ₁	890.94508	49.2 (1)	896.05360	51.9 (1)			50.8
2,4,6-trinitrotoluene								
Nitro	C ₁	875.08818	0.0 (0)	880.12509	0.0 (0)			0.0
<i>aci</i> -Nitro	C ₁	875.05483	20.9 (0)	880.06162	39.8 (0)			39.5
TS	C ₁	875.00275	53.6 (1)	880.02077	65.5 (1)			65.3

SECTION VII

CYCLIZATIONS REACTIONS OF SUBSTITUTED NITROETHYLENES

1. INTRODUCTION

In the context of unraveling the intricacies that underlie the combustion mechanisms of less sensitive nitroaromatic explosives, it is of importance to determine the key intermediates that would trigger such a process. The charge of this contract research was to establish whether or not nitronic acids are viable candidates to occupy such a central role. This was answered in the above sections. Here logical next steps are explored. If the nitronic acids play indeed a pivotal role it follows that their decomposition pathways must be energetically competitive with those that involve the nitroaromatics directly. The two processes that were further investigated are bond dissociation energies and cyclization reactions to alternative products. These studies were conducted beyond the contract charge to probe future directions to determine in greater detail the combustion mechanism of polynitroaromatics.

2. BOND DISSOCIATION ENERGIES

A large spectrum of radicals that constitute fragments of simple nitroalkanes and substituted nitroalkenes was calculated. These were all fully optimized and characterized at various levels of theory. Table 13 summarizes the energy data and also lists the $\langle S^2, 1 \rangle$ data which underscore that not all radicals were calculated satisfactorily as identified by their significant deviations from 0.75. It is recognized that more sophisticated levels of theory (e.g. MRCI) are required to accurately calculate bond dissociation energies in particular for the nitroso radicals for which various electronic states can be envisioned. Nevertheless, some insight may be obtained from the listed data. Several combinations can be made to obtain crude estimates for various bond dissociation energies. We concentrate only on the nitro and nitronic acid groups as summarized in Tables 14-17. The C-NO₂ bond dissociation energies of nitromethane and nitroethane are remarkably similar to the experimentally determined values. The C-NO₂ bond dissociation energy increases by introducing a double bond that is conjugated to the nitro group, i.e. nitroethylene. Even larger values are obtained for the hydroxy and amino substituted olefins (see Table 14). These data suggest that in the absence of steric effects the C-NO₂ bond is strengthened by conjugative effects.

The (O)N-OH bond dissociation energies of the nitronic acids of the substituted nitroethylenes, listed in Table 17, underscore that inadequate levels of theory have been employed. The data do suggest that PMP2/6-31G* overestimates the bonding energies and that the N-OH bond is likely to be weak, but this must be verified at more sophisticated levels of theory. It is plausible, however, that the nitronic acids are likely candidates to generate nitroso compounds, which are experimentally abundant products in the decompositions of nitroaromatics.

TABLE 13. ABSOLUTE ENERGIES (in hartrees) OF NITROMETHANE, NITROETHANE, NITROETHYLENE, SUBSTITUTED NITROETHYLENE, AND THEIR FRAGMENTS.

Molecule	Sym.	UHF/3-21G	UHF/6-31G*	PMP2/6-31G*	PMP4/6-31G**	ZPE ^b	I ^c	S ^{2,d}
CH ₃ NO ₂	C _s	-242.25586	-243.66199	-244.34534	-244.37427	30.80	0	-
C ₂ H ₃ NO ₂	C _s	-279.88906	-281.50409	-282.31131	-282.34769	34.00	0	-
C ₂ H ₅ NO ₂	C _s	-281.08265	-282.70109	-283.52047	-283.55884	48.28	0	-
HO-CH=CH-NO ₂	C _s	-354.34455	-356.37129	-357.36070	-357.39829	37.85	0	-
H ₂ N-CH=CH-NO ₂	C _s	-334.63553	-336.54755	-337.52181	-337.56267	44.86	0	-
H ₃ C-CH=CH-NO ₂	C _s	-318.71225	-320.54169	-321.48544	-321.53231	51.15	0	-
O=CH-CH=NO ₂ H	C _s	-354.33883	-356.35703	-357.35329	-357.38967	37.29	0	-
HN=CH-CH=NO ₂ H	C _s	-334.61206	-336.51574	-337.49950	-337.53963	44.87	0	-
H ₂ C=CH-CH=NO ₂ H	C _s	-318.71557	-320.51239	-321.45489	-321.50247	51.12	0	-
HO*	C _s	-74.97023	-75.38228	-75.52475	-75.53695	5.15	0	0.75
NO ₂ *	C _s	-202.8435	-204.03149	-204.57253	-204.59027	5.56	0	0.76
CH ₃ *	C _s	-39.34261	-39.55899	-39.67504	-39.69056	17.50	0	0.75
CHO*	C _s	-112.60380	-113.47660	-113.54277	-113.55751	8.12	0	0.76
CH ₂ N*	C _s	-92.86450	-93.39296	-93.66420	-93.68376	14.67	0	0.79
CH ₂ NO ₂ *	C _s	-241.61810	-242.98587	-243.62084	-243.64652	21.53	0	1.12
C ₂ H ₃ *	C _s	-76.96280	-77.39029	-77.62332	-77.64605	21.85	0	0.89
C ₂ H ₅ *	C _s	-78.16365	-78.59715	-78.84679	-78.87368	35.70	0	0.75
C ₂ H ₂ O:	C _s	-150.72351	-151.58631	-151.99331	-152.02453	17.71	0	-
C ₂ H ₃ N:	C _s	-131.00487	-131.75694	-132.15135	-132.18727	25.54	0	-
C ₂ H ₃ O*	C _s	-151.39772	-152.24291	-152.65714	-152.68242	25.11	0	0.87
C ₂ H ₄ N*	C _s	-131.68236	-132.41496	-132.81670	-132.84628	32.44	0	0.88
C ₂ H ₂ NO ₂ *	C _s	-279.38148	-280.96491	-281.72012	-281.75418	24.41	0	0.99
C ₂ H ₃ N ₂ O*	C ₁	-259.63907	-261.11555	-261.85738	-261.89768	33.07	0	0.89
C ₃ H ₄ :	C _s	-115.12652	-115.77656	-116.14060	-116.17728	32.62	0	-
C ₃ H ₅ *	C _s	-115.78488	-116.42915	-116.79742	-116.83097	39.47	0	0.88
C ₃ H ₄ NO*	C _s	-243.76104	-245.13364	-245.83927	-245.88786	38.03	0	1.15
HO ₂ N:(trans)	C _s	-203.46601	-204.63768	-205.17335	-205.19587	13.03	0	-
HO ₂ N:(cis)	C _s	-203.46850	-204.63994	-205.17536	-205.19787	13.08	0	-

* PMP4(SDTQ)/6-31G**//MP2/6-31G*. ^b Zero-point energies scaled by 0.9.

^c Number of imaginary frequencies. ^d After annihilation at PMP2/6-31G*

TABLE 14. C-NO₂ BOND DISSOCIATION ENERGIES (in kcal/mol) FOR SELECTED NITROALKANES AND SUBSTITUTED NITROETHYLENES.

Compound	UHF/3-21G	UHF/6-31G*	PMP2/6-31G*	PMP4/6-31G**		Expt.
				rel.	(+ZPE)	
CH ₃ -NO ₂	43.8	44.9	61.3	58.6	50.8	60.1
CH ₃ CH ₂ -NO ₂	46.8	45.5	63.5	59.5	52.5	60.5
CH ₂ =CH-NO	52.0	51.6	72.5	69.9	63.3	
HO-CH=CH-NO ₂	64.9	60.8	82.2	78.8	72.4	
H ₂ N-CH=CH-NO ₂	68.9	63.5	83.2	79.1	72.3	
H ₃ C-CH=CH-NO ₂	52.7	50.9	72.5	69.7	63.6	

* Relative energies in the second column are corrected for zero-point energies.

TABLE 15. C-C BOND DISSOCIATION ENERGIES (in kcal/mol) FOR SUBSTITUTED *anti*-NITROETHYLENES.

Compound	UHF/3-21G	UHF/6-31G*	PMP2/6-31G*	PMP4/6-31G**	
				rel.	(+ZPE)
HO-CH=CH-NO ₂	73.4	77.5	119.0	116.5	108.5
H ₂ N-CH=CH-NO ₂	81.2	85.9	134.6	131.4	122.3
H ₃ C-CH=CH-NO ₂	84.5	85.5	132.3	131.7	124.0

* Relative energies in the second column are corrected for zero-point energies.

TABLE 16. C=N BOND DISSOCIATION ENERGIES (in kcal/mol) FOR SUBSTITUTED *aci*-NITROETHYLENES.

Compound	UHF/3-21G	UHF/6-31G*	PMP2/6-31G*	PMP4/6-31G**
			rel.	(+ZPE)
HO-CH=CH-NO ₂	93.7	83.5	117.1	105.0
H ₂ N-CH=CH-NO ₂	88.9	76.0	109.7	96.9
H ₃ C-CH=CH-NO ₂	75.7	60.5	87.2	79.9
				74.5

* Relative energies in the second column are corrected for zero-point energies.

TABLE 17. N-OH BOND DISSOCIATION ENERGIES (in kcal/mol) FOR SUBSTITUTED *aci*-NITROETHYLENES.

Compound	UHF/3-21G	UHF/6-31G*	PMP2/6-31G*	PMP4/6-31G**
			rel.	(+ZPE)
HO-CH=CH-NO ₂	-8.1	6.2	68.0	61.8
H ₂ N-CH=CH-NO ₂	1.7	11.2	73.7	65.9
H ₃ C-CH=CH-NO ₂	-9.1	-2.2	57.0	48.7
				40.8

* Relative energies in the second column are corrected for zero-point energies.

3. CYCLIZATION REACTIONS

The objective of the model study described in this section was to elaborate a pathway that could mimic possible formation of anthranilic acid from nitroaromatics by means of nitronic acids. Such pathways can be elaborated by both radical and acid/base mechanisms. In either case, the involvement of nitronic acids would be an important component. Therefore, valuable information with respect to the integrity of nitronic acids was sought.

We considered the lowest energy pathway for cyclization of nitrovinyl alcohol (16), nitrovinyl amine (21), and 3-nitropropene (26) via non-ionic and non-radical routes. The total and relative HF/3-21G, HF/6-31G*, and MP2/6-31G* energies of the various feasible intermediates and associated transition structures are listed in Table 18-20, respectively. The pathways are depicted schematically in the corresponding Figures 24-26, which display the structures and the MP2 energy profiles for the cyclization reactions. There is some necessary overlap with Section III.

Cyclization is feasible for 2-nitrovinyl amine and 1-nitropropene whose products can undergo dehydration, which in both cases renders the entire reaction scheme exothermic at the correlated level of theory. This exothermicity is largest for 1-nitropropene, which also has the lower energy barriers for the primary cyclization reaction, i.e. 49.7 kcal/mol vs 66.3 kcal/mol relative to 21 and 26, respectively. No cyclization product could be found at the correlated level for 2-nitrovinyl alcohol, (at HF/6-31G* a cyclic structure was obtained with an associated barrier for formation of 88.5 kcal/mol, relative to 16). While it is recognized that the peroxy group is theoretically difficult to calculate accurately, the large endothermicity makes cyclization an unlikely prospect. This is also the case for the cyclization of 2-nitrovinyl amine which is endothermic by 61.3 kcal/mol. However, the cyclization product and the nitronic acids of 1-nitropropene are nearly of the same energy and only 15-20 kcal/mol less stable than 26, with corresponding similar transformation barriers of 42-50 kcal/mol.

The reaction profiles illustrate that cyclization of 1-nitropropene is feasible and this compares well with the experimentally observed anthranilic acids. Cyclization of 2-nitrovinyl amine is possible but may be energetically prohibitive with little kinetic stability of the product. Cyclization of 2-nitrovinyl alcohol appears not to be feasible.

Because of the relation with the nitroaromatics it is of interest to briefly compare the various nitronic acid conformations. As demonstrated in Sections IV-VI all aromatic nitronic acids have a cis conformation of the $O\leftarrow N-O-H$ group; it was shown in Section IV, Table 10 and Figures 13 and 16, that the trans conformations have no kinetic stability. In the case of the ethylenes the kinetic stability of the cis forms (32 and 38) are 8-10 kcal/mol less stable (barrier ca. 15 kcal/mol) than the corresponding trans forms (17 and 22). Interestingly, in all three systems (2-nitrovinyl alcohol, 2-nitrovinyl amine, and 1-nitropropene) the nitronic acids with the N-OH farthest from the substituent (34, 40, and 45) are the most stable cis $O\leftarrow N-O-H$ conformers. These have also significant kinetic stability, although under experimental conditions (liquid, solid) such transformations may occur ionically (Section II). It is then relevant to note that these nitronic acids 34, 40, and 45 are 'only' 11.3, 22.4, and 18.0 kcal/mol less stable than their corresponding most stable tautomers. Especially the relative order is of interest as it compares well with that calculated for picric acid, picramide, and TNT.

TABLE 18. TOTAL (in hartrees) AND RELATIVE (in kcal/mol) ENERGIES OF INTERMEDIATES AND TRANSITION STRUCTURES FOR THE CYCLIZATION OF 2-NITROETHENOL.

Structures	Sym.	HF/3-21G		HF/6-31G*		MP2/6-31G*	
		abs.	rel.	abs.	rel.	abs.	rel.
C₂H₃NO₂							
16	C _s	-354.34455	0.0	-356.37129	0.0	-357.36070	0.0
18 (16 → 17)	C _s	-354.33310	7.2	-356.34804	14.0	-357.34911	7.3
17	C _s	-354.33883	3.6	-356.35703	8.9	-357.35329	4.7
31 (17 → 32)	C _s	-354.32119	14.2	-356.33876	20.4	-357.33133	18.4
32	C _s	-354.33333	7.0	-356.34941	13.7	-357.34040	12.7
33 (32 → 34)	C _s	-354.29237	32.7	-356.29333	48.9	-357.29547	40.9
34	C _s	-354.33411	6.5	-356.34947	13.7	-357.34262	11.3
35 (34 → 36)	C ₁	-354.24547	62.2	-356.23025	88.5		
36	C ₁	-354.29131	33.4	-356.25689	71.8		

TABLE 19. TOTAL (in hartrees) AND RELATIVE (in kcal/mol) ENERGIES OF INTERMEDIATES AND TRANSITION STRUCTURES FOR THE CYCLIZATION OF 2-NITROVINYLAMINE.

Structures	Sym.	HF/3-21G		HF/6-31G*		MP2/6-31G*	
		abs.	rel.	abs.	rel.	abs.	rel.
C₂H₄N₂O₂							
21	C _s	-334.63553	0.0	-336.54755	0.0	-337.52181	0.0
23 (21 → 22)	C _s	-334.61017	15.9	-336.50763	25.1	-337.49748	15.3
22	C _s	-334.61206	14.7	-336.51574	19.9	-337.49950	14.0
37 (22 → 38)	C _s	-334.59238	27.1	-336.49782	31.2	-337.47537	29.1
38	C _s	-334.60233	20.8	-336.50685	23.5	-337.48295	24.4
39 (38 → 40)	C _s	-334.56441	44.6	-336.45321	59.2	-337.43985	51.4
40	C _s	-334.60294	20.5	-336.50700	25.5	-337.48612	22.4
41 (40 → 42)	C ₁	-334.52723	67.9	-336.40669	88.4	-337.41616	66.3
42	C ₁	-334.58858	29.5	-336.45978	55.1	-337.42408	61.3
43	C _s	-259.06708		-260.54385		-261.33605	
H₂O	C _s	-75.58596		-76.01075		-76.19685	
Δ(42 → 43)			-40.5		-61.7		-68.3

TABLE 20. TOTAL (in hartrees) AND RELATIVE (in kcal/mol) ENERGIES OF INTERMEDIATES AND TRANSITION STRUCTURES FOR THE CYCLIZATION OF 1-NITROPROPENE.

Structures	Sym.	HF/3-21G		HF/6-31G*		MP2/6-31G*	
		abs.	rel.	abs.	rel.	abs.	rel.
$C_3H_5NO_2$							
26	C_s	-318.71225	0.0	-320.54169	0.0	-321.48544	0.0
28 (26 → 27)	C_s	-318.64118	44.6	-320.44925	58.0	-321.41821	42.2
27	C_s	-318.71557	-2.1	-320.51239	18.4	-321.45489	19.2
44 (27 → 45)	C_s	-318.68262	18.6	-320.46408	48.7	-321.40995	47.4
45	C_s	-318.72281	-6.6	-320.51789	14.9	-321.46039	15.7
46 (45 → 47)	C_1	-318.66661	28.6	-320.44728	59.2	-321.40630	49.7
47	C_1	-318.75295	-25.5	-320.53116	6.6	-321.45667	18.0
48	C_s	-243.21070		-244.58850		-245.33411	
H_2O	C_s	-75.58596		-76.01075		-76.19685	
$\Delta(42 \rightarrow 43)$			-27.4		-42.7		-46.6

Tautomerism and Cyclization of β -Nitroethanol

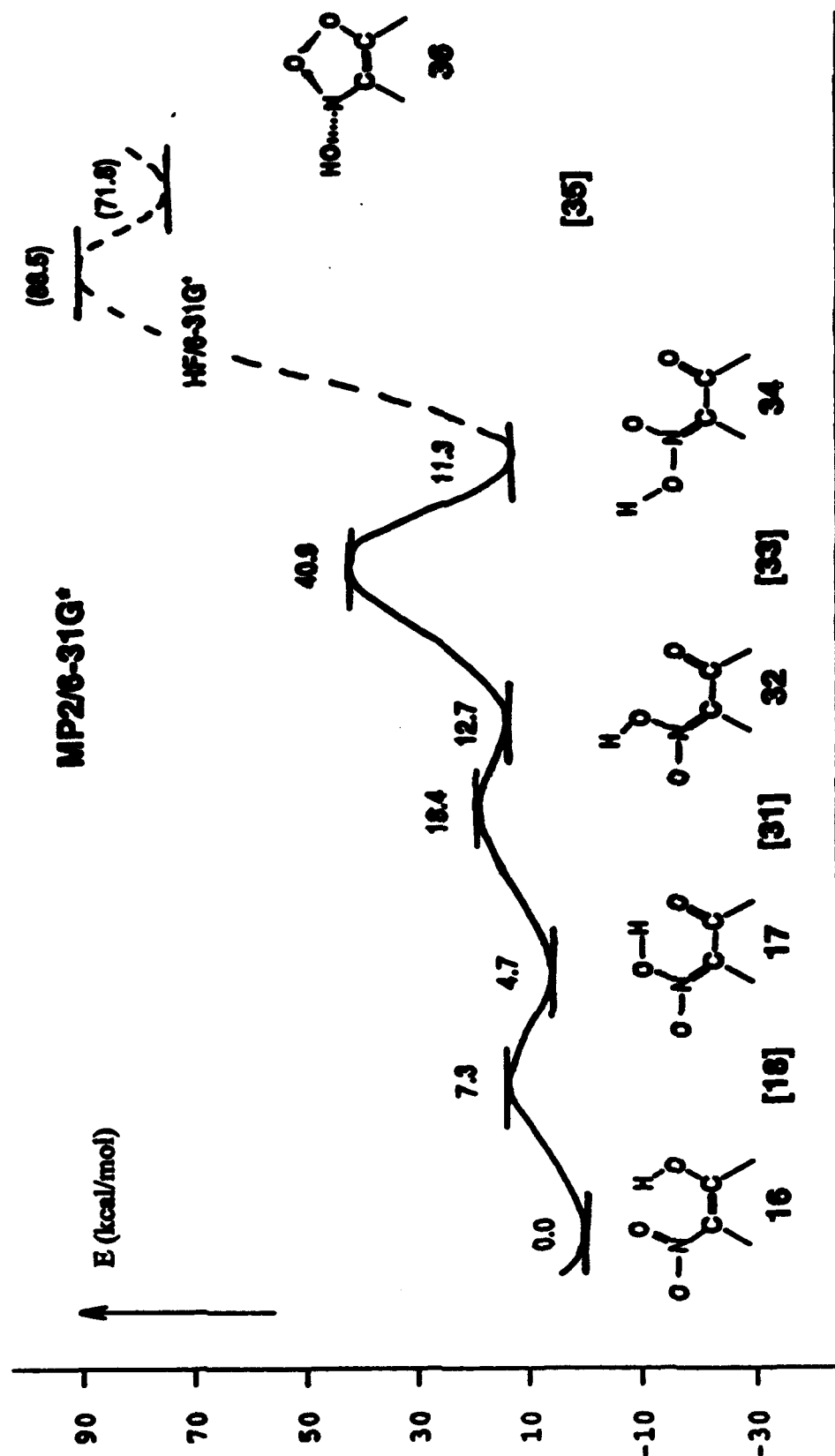


Figure 24. Energy Profile for the Tautomerism and Cyclization of β -Nitroethanol.

Tautomerism and Cyclization of β -Nitrovinylamine

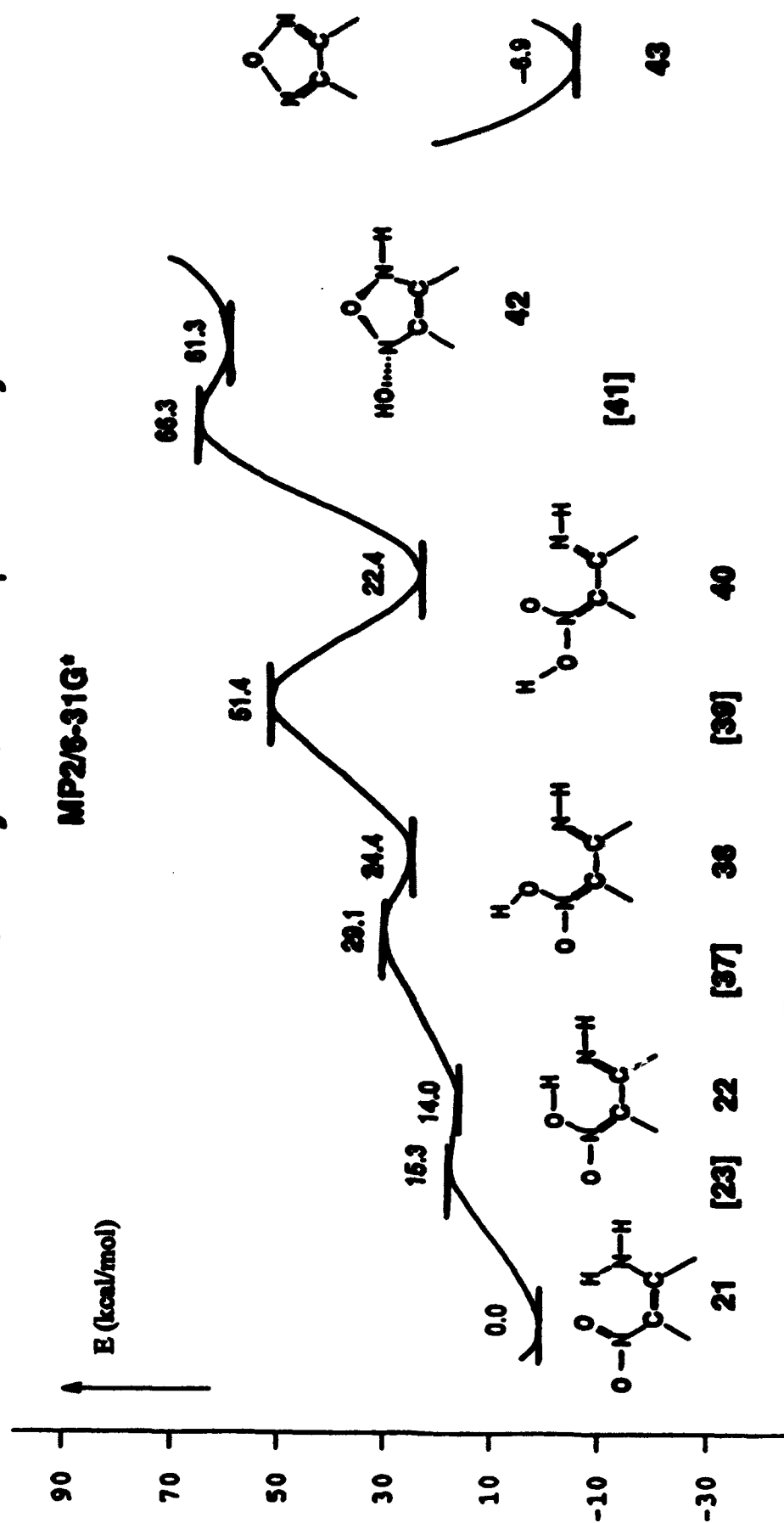


Figure 25. Energy Profile for the Tautomerism and Cyclization of β -Nitrovinylamine.

Tautomerism and Cyclization of 1-Nitropropene

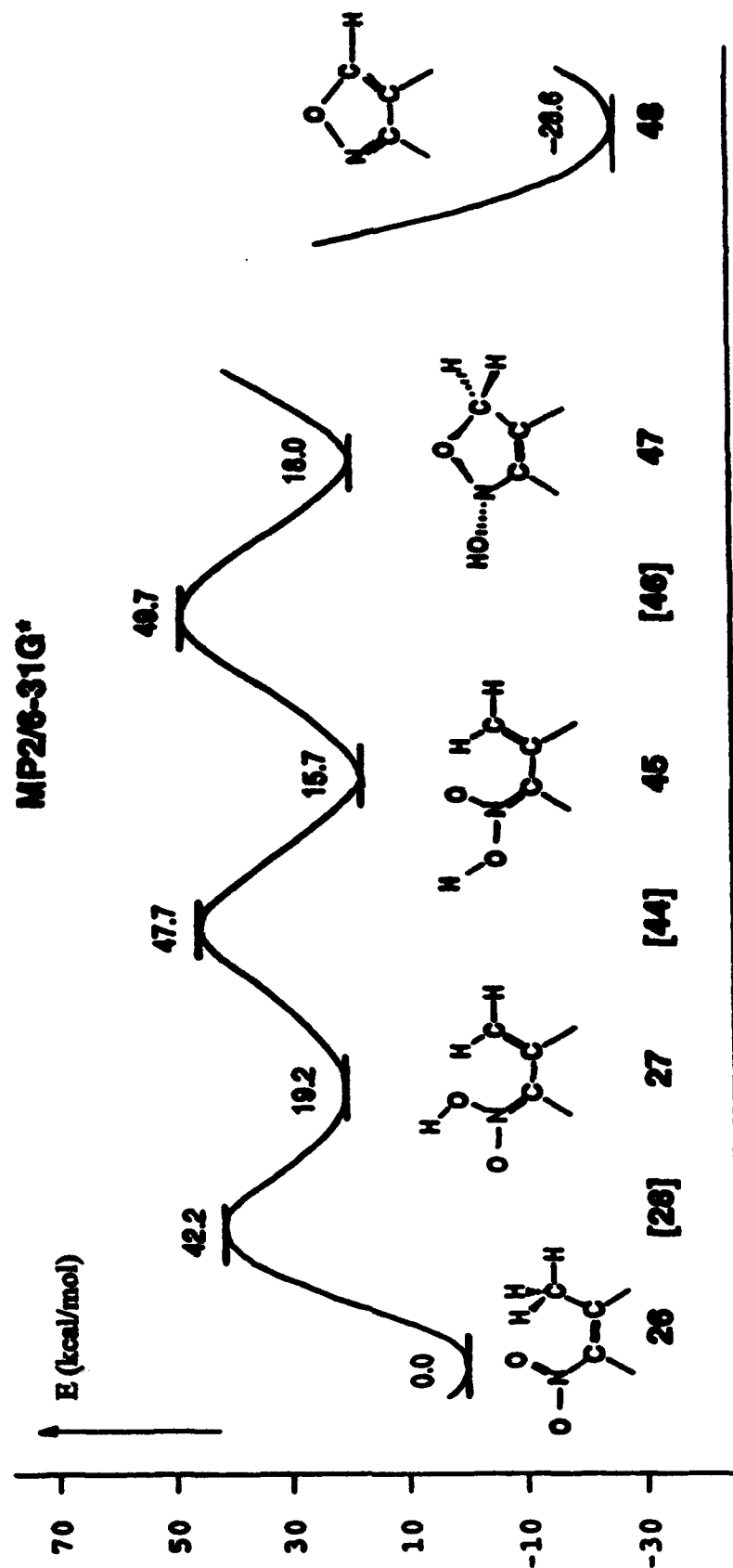


Figure 26. Energy Profile for the Tautomerism and Cyclization of 1-Nitropropene.

SECTION VIII

SUMMARY AND CONCLUSIONS

In this project we have demonstrated the viability of nitronic acids in the smallest alkanes, alkenes, and aromatics.

The parent nitro \rightleftharpoons *aci*-nitro, keto \rightleftharpoons enol, and imine \rightleftharpoons enamine tautomeric processes were investigated at various levels of theory, including G1. The energy difference between the tautomeric pairs reduces significantly when large basis sets are used in conjunction with extensive inclusion of electron correlation effects.

Tautomerism is enhanced in the conjugated systems which were calculated at MP4/6-31G*. These systems allow for intramolecular [1,5]-H transfers. Hydrogen bonding is present in the 2-nitrovinyl alcohol and amine and their nitronic acids have trans O \leftarrow N-O-H conformations. In contrast, that of 1-nitropropene has a *cis* form. The energy differences of the nitroethylenes with the *cis* nitronic acids are much larger. Cyclization of 1-nitropropene can occur via its *aci*-nitro tautomer and is exothermic after dehydration. Cyclization of nitrovinyl amine (via a trans nitronic acid) is less likely and not possible for the alcohol. In these cases decomposition is more likely as the N-OH bond is relatively weak.

Tautomerism in *ortho*-substituted nitrobenzenes is a [1,5]-H transfer process that leads exclusively to nitronic acids with a *cis* O \leftarrow N-O-H conformation. These systems were calculated at MP2/6-31G*. The energy differences between the nitro and *aci*-nitro tautomers are significant with the smallest difference for *o*-nitrophenol and the largest for *o*-nitrotoluene. The nitronic acids have sizable kinetic stabilities.

Tautomerism in CH₃-, NH₂-, and OH- substituted 2,6-dinitrobenzenes, calculated at HF/6-31G*, is similar to that in the mononitro derivatives with subtle differences. The buttressing effect of the two nitro groups enhances tautomerism in the phenol and toluene derivatives, but hampers that in the aniline derivative possibly because of the double H-bonding of the amine group.

Tautomerism in picric acid, picramide, and TNT was calculated at HF/6-31G* at which level the nitronic acids have significant kinetic stabilities. With the additional polarizing 4-nitro group the energy difference between the tautomers (and barriers) is reduced further for the phenol and toluene derivatives but increases for the aniline analogue. Tautomerism is by far the easiest for picric acid, (which is experimentally also the most sensitive to impact of the three), with an energy difference of 25 kcal/mol and a barrier of 34 kcal/mol. The nitronic acids of picramide and TNT are significantly less stable, i.e. 48 and 39 kcal/mol, respectively, but follow the experimental sensitivity order of these compounds. MP2 correction on the [1,5]-H transfer barrier for tautomerism of TNT gives a value of 52 kcal/mol which is similar to the experimental induction activation for thermal decomposition.

These studies demonstrate, conform to experiment, that picric acid by means of its nitronic acid is more sensitive than picramide and TNT. The theoretical energies on the latter compare with experimental data. The studies also show that high levels of theory are needed for accurate calculations. They further establish that competing decompositions may exist for TNT and must exist for picramide.

SECTION IX

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